

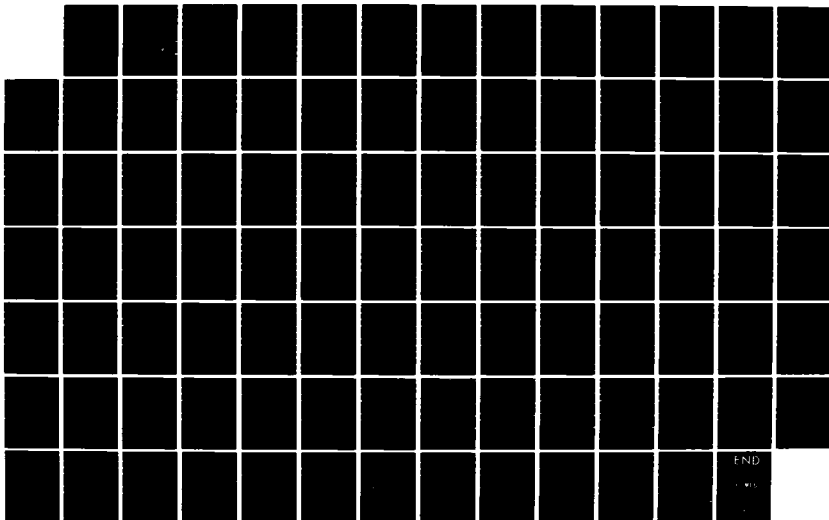
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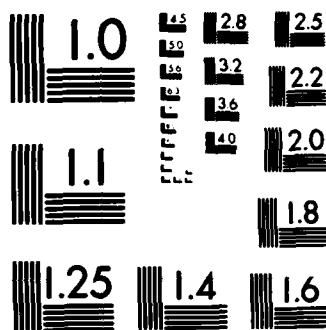
DIAGRAMS OF CHEMICAL AND ELECTROCHEMICAL EQUILIBRIA IN
THE PRESENCE OF OX. (U) CENTRE BELGE D'ETUDE DE LA
CORROSION BRUSSELS M POURBAIX NOV 84 EOARD-TR-85-04
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DIAGRAMS OF CHEMICAL AND ELECTROCHEMICAL EQUILIBRIA IN THE PRESENCE OF
OXYGEN AND SULPHUR.

Grant: AFOSR-84-0141

for the E.O.A.R.D, 223 Old Marylebone Road, London NW1 5TH, England

Principal Investigator: Prof. Dr. Ing. Marcel POURBAIX

Final Report, November 1984.

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RAPPORTS TECHNIQUES

RT. 283 - Equilibres chimiques et électrochimiques en présence d'une phase gazeuse. 12. Soufre-fer.

par ZHANG Zhongcheng, ZHANG Heming, YANG Xizhen et Marcel POURBAIX

Résumé:

En se basant sur des données thermodynamiques publiées, on établit des diagrammes qui représentent l'influence de la température et de la pression sur les conditions d'équilibre de l'ensemble de 20 réactions auxquelles peuvent participer les 18 substances suivantes:

- substances solides: $S\alpha$, $S\beta$, $Fe\alpha$, $Fe\gamma$, $Fe\delta$, $FeS\beta,\gamma$ (troilite), $FeS_{1+x}\beta$ (pyrrhotite hexagonale basse température), $FeS_{1+x}\gamma$ (pyrrhotite hexagonale haute température), FeS_2 (pyrite)
- substances liquides: S , Fe , FeS , FeS_{1+x}
- substances gazeuses: (S_1) , (S_2) , (Fe) , (FeS) .

On applique ces diagrammes à l'étude de l'influence de la température et de la pression sur la stabilité de la troilite et de la pyrite et sur la stabilité et la composition de la pyrrhotite hexagonale haute température $FeS_{1+x}\gamma$.

Il est très probable que la volatilisation du sulfure ferreux qui se produit par chauffage résulte, non pas de la formation du sulfure ferreux gazeux (FeS), mais de sa décomposition avec formation de (Fe) , (S_2) et (S_1) gazeux. Les données thermodynamiques actuellement admises pour (FeS) gazeux sont donc probablement inexactes et devraient être corrigées.

Mots-clefs:

Equilibres chimiques - équilibres électrochimiques - potentiels d'électrode (par rapport à une électrode de référence à soufre standard E_{ess}) - soufre - fer - troilite - pyrrhotite - pyrite.

→ RT. 283 - Chemical and electrochemical equilibria in the presence of a gaseous phase. 12. Sulphur - iron.

by ZHANG Zhongchen, ZHANG Heming, YANG Xizhen and Marcel POURBAIX.

Summary:

→ On the basis of published thermodynamic data, one establishes diagrams representing the influence of temperature and pressure on the equilibrium conditions of the whole of 20 reactions, where the 18 following substances may take part:

- solid substances: $\alpha, \beta S$ (sulphur), $\alpha, \gamma, \delta Fe$ (iron), $\beta, \gamma FeS$ (troilite), $\beta, \gamma FeS_{1+x}$ (pyrrhotite), FeS_2 (pyrite),
- liquid substances: S , Fe , FeS , FeS_{1+x}
- gaseous substances: (S_1) , (S_2) , (Fe) , (FeS) .

→ These diagrams are applied to the study of the influence of temperature and pressure on the stability of troilite FeS and pyrite FeS_2 , and on the stabi-

gamma

lity and composition of high temperature hexagonal pyrrhotite FeS_{1+x} and of molten ferrous sulphide.

It is most likely that the volatilisation of ferrous sulphide which occurs by heating does not result in the formation of gaseous (FeS) , but in its decomposition with formation of (Fe) , (S_2) and (S_1) . The thermodynamic data presently admitted for gaseous (FeS) are thus probably wrong and should be revised.

Key-words: Cont'd

Chemical equilibria - electrochemical equilibria - equilibrium diagrams, electrode potentials' (versus a standard sulphur reference electrode Esse) sulphur - iron - troilite - pyrrhotite - pyrite.

Esusse

RT. 284 - Equilibres chimiques et électrochimiques en présence d'une phase gazeuse. 13. Oxygène - soufre - fer.

par YANG Xizhen, ZHANG Heming, ZHANG Zhongcheng et Marcel POURBAIX.

Résumé:

En se basant sur des données thermodynamiques publiées, on établit des diagrammes qui représentent l'influence de la température et de la pression sur les conditions d'équilibre de l'ensemble de 48 réactions auxquelles peuvent participer les 40 substances suivantes:

- substances solides: O_2 , O_3 , αS , βS , αFe , γFe , δFe , Fe_{1-x}O , Fe_3O_4 , $\text{Fe}_{3-y}\text{O}_4$, Fe_2O_3 , SO_2 , SO_3 , $\beta\text{, } \gamma\text{FeS}$, FeS_{1+x} , $\beta\text{, } \gamma\text{FeS}_{1+x}$, FeS_2 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$
- substances liquides: O_2 , S , Fe , Fe_{1-x}O , $\text{Fe}_{3-y}\text{O}_4$, Fe_2O_3 , FeS , FeS_{1+x}
- substances gazeuses: (O_1) , (O_2) , (O_3) , (S_1) , (S_2) , (S_6) , (S_8) , (Fe) , (S_{20}) , (SO) , (SO_2) , (SO_3) .

On applique ces diagrammes à l'étude de l'influence de la température et de la pression sur la stabilité et la décomposition de FeSO_4 et $\text{Fe}_2(\text{SO}_4)_3$, sur l'action catalytique de l'oxyde ferrique sur l'oxydation du (SO_2) en (SO_3) et sur la corrosion à haute température du fer en présence d'atmosphères gazeuses contenant des dérivés de l'oxygène et du soufre.

Mots-clefs:

Equilibres chimiques - équilibres électrochimiques - potentiels d'équilibre - catalyse - sulfate ferreux - sulfate ferrique - corrosion à haute température.

RT. 284 - Chemical and electrochemical equilibria in the presence of a gaseous phase. 13. Oxygen - sulphur - iron.

by YANG Xizhen, ZHANG Heming, ZHANG Zhongcheng and Marcel POURBAIX.

Summary:

On the basis of published thermodynamic data, one establishes diagrams representing the influence of temperature and pressure on the equilibrium conditions of the whole of 48 reactions, where the 40 following substances may take part:

- solid substances: O_2 , O_3 , αS , βS , αFe , γFe , δFe , Fe_{1-x}O , Fe_3O_4 , $\text{Fe}_{3-y}\text{O}_4$, Fe_2O_3 , SO_2 , αSO_3 , $\beta\text{, } \gamma\text{FeS}$, $\beta\text{, } \gamma\text{FeS}_{1+x}$, FeS_2 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$
- liquid substances: O_2 , S , Fe , Fe_{1-x}O , $\text{Fe}_{3-y}\text{O}_4$, Fe_2O_3 , FeS , FeS_{1+x}
- gaseous substances: (O_1) , (O_2) , (O_3) , (S_1) , (S_2) , (S_6) , (S_8) , (Fe) , (S_{20}) , (SO) , (SO_2) , (SO_3) .

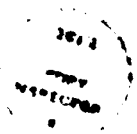
1-11d
These diagrams are applied to the study of the influence of temperature and pressure on the stability and decomposition of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, on the ferric oxide as a catalyst for the oxidation of (SO_2) to (SO_3) , and on the high temperature corrosion of iron in gaseous atmospheres containing oxygen and sulphur derivatives. Originator Supplied keywords include:

Key-words:

Chemical equilibria, electrochemical equilibria, equilibrium potentials, catalysis, ferrous sulphate, ferric sulphate, high temperature corrosion,

cont'd on p. 11

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CHEMICAL AND ELECTROCHEMICAL EQUILIBRIA
IN THE PRESENCE OF A GASEOUS PHASE *

S-Fe 12. SULPHUR-IRON

by

ZHANG Zhongcheng**, ZHANG Heming**, YANG Xizhen**
and Marcel POURBAIX***

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* The present work is a continuation of similar work relating to systems O, H, O-Fe, O-H, O-H-Fe, C, O-C, O-C-Fe, S and O-S (see ref. (1) and (2) pp.59 - 89)

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1. SUBSTANCES CONSIDERED AND NOT CONSIDERED

	<u>Considered</u>	<u>Not considered</u>
<u>Solid substances</u>	αS (rhombic) βS (monoclinic) $\alpha, \gamma, \delta Fe$ $\theta, \gamma FeS$ (troilite) $\alpha, \beta, \gamma FeS_{1+x}$ (pyrrhotite) $\alpha, \beta, \gamma FeS_{1.140}$ (or $Fe_{0.877}S$) FeS_2 (pyrite)	FeS_2 (marcasite)
<u>Liquid substances</u>	S Fe FeS FeS_{1+x}	
<u>Gaseous substances</u>	$(S_1), (S_2)$ (Fe) (FeS)	$(S_3), (S_4), (S_5),$ $(S_6), (S_7), (S_8)$

2. TEMPERATURES AND ENTHALPIES OF TRANSFORMATION OF THE CONSIDERED CONDENSED SUBSTANCES.

	Equilibrium temperatures $T(^{\circ}K)$	Enthalpies of transformation $\Delta H(\text{calories.mole}^{-1})$	ref.
$\alpha S/\beta S$	368.3	95.7	(3), p.930
$\beta S/S$	388.4	412.8	(3), p.931
$\alpha Fe/\gamma Fe$	1184	215	(3), p.828
$\gamma Fe/\delta Fe$	1665	200	(3), p.828
$\delta Fe/Fe$	1809	3300	"
$\theta Fe_{0.877}S/\gamma Fe_{0.877}S$	598	95	(3), p.834
or $\beta FeS_{1.140}/\gamma FeS_{1.140}$	"	108	"

<u>Triple points</u>	Equilibrium temperature($^{\circ}K$)	Equilibrium electrode potentials E_{sse} (mv)
A. $FeS_2/\beta FeS_{1+x}/\gamma FeS_{1+x}$	598	-310*
B. $FeS_2/S/\gamma FeS_{1+x}$	1020?	+40*

C. $\gamma\text{FeS}_{1+x}/\text{S}/\text{FeS}_{1+x}$	1210?	+100*
E. $\gamma\text{FeS}_{1+x}/\gamma\text{Fe}/\text{FeS}_{1+x}$	1261	-430*
F. $\gamma\text{FeS}/\alpha\text{Fe}/\gamma\text{Fe}$	1184	-450*
G. $\delta\text{FeS}/\gamma\text{FeS}/\alpha\text{Fe}$	598	-610*
H. $\gamma\text{Fe}/\delta\text{Fe}/\text{FeS}_{1+x}$	1665	-410*

3. THERMODYNAMIC DATA

3.1. Standard chemical potentials μ° (or standard free enthalpies of formation ΔG_f°) (tables I and II)

Table I (page 24) gives, for different temperatures from zero till 6000°K, values of standard chemical potentials admitted for the substances considered in the present work. All values in table I are given by the JANAF tables(ref.(3)). However, as the degree of sulphidation of iron sulphides increases according to the order FeS , $\text{Fe}_{0.877}\text{S}$ and FeS_2 , we have changed $\text{Fe}_{0.877}\text{S}$ into $\text{FeS}_{1.140}$, so that this order appears as FeS , $\text{FeS}_{1.140}$ and FeS_2 . The values of $\mu_{\text{FeS}_{0.877}}^\circ$ given by JANAF have thus been changed into corresponding values for $\text{FeS}_{1.140}$.

The values of standard chemical potentials μ° given in table I will be used throughout the present work for the calculation of the equilibrium diagrams. Some of these values should be considered as provisional and subject to improvement.

3.2 Reactions and equilibria considered

Formulation of the standard free enthalpies of reaction ΔG_r° (table II)

In the present work, relating to the sulphur-iron system, we intend to establish equilibrium diagrams as a function of the free enthalpy of reaction per mole of biatomic gaseous sulphur, $RT \ln p_{\text{S}_2}$, as well as of the electrode potential versus a standard

* These values are given by a graphical method according to figure 11 of present report (see page 45).

sulphur electrode, E_{sse} (which would operate reversibly under $p_{S_2} = 1$ atm), and the decimal logarithms of the partial pressure of gaseous sulphur ($\log p_{S_2}$). We have thus arbitrarily chosen (S_2) as the reference gaseous species for the sulphur-iron system, and we shall write all reactions to which sulphur participates, whatever its form, in such a way that one mole of gaseous (S_2) intervenes among the reactants.

Table II (page 25) gives a list of 20 reactions and formulae which will be used for calculating the equilibrium conditions, and which refer successively to the one component system sulphur (with the mark \diamond), to the one component system iron (with the mark \bigcirc) and to the two components system sulphur-iron (with the mark \bigcirc).

3.3. Equilibrium conditions of the considered reactions (tables III and IV)

The equilibrium conditions of all reactions to which gaseous (S_2) participates are calculated by the following formulae:

$$\Delta G_r^*(\text{cal.}) = \sum \nu \mu^* = RT \ln p_{S_2}$$

$$E_{sse}(\text{mv}) = \Delta G_r^*/92.242$$

$$\log p_{S_2}(\text{atm}) = \Delta G_r^*/4.5756/T$$

From tables I and II, we have calculated the values of ΔG_r^* of the considered reactions relating to S-Fe system, the values of E_{sse} , and the corresponding logarithms of the equilibrium partial pressures of (S_2). These values are given in table III (pages 26 to 29).

According to table III, one obtains table IV (pages 31 to 35) which gives approximate formulae for the free enthalpies of reaction ΔG_r^* (calories per mole (S_2)) of the considered reactions, for different temperature-ranges as well as the corresponding formulae for the values of the electrode potential E_{sse} and of the logarithms of the partial pressures of (S_2).

for instance:

for reaction (1) : $2\text{Fe} + (S_2) = 2 \text{FeS}$

$$\Delta G_r^* = 2 \mu_{\text{FeS}}^* - 2 \mu_{\text{Fe}}^* - \mu_{(S_2)}^*$$

$$RT \ln p_{S_2}^* = \Delta G_r^* \quad \text{and} \quad E_{sse}^* = \Delta G_r^*/92.242$$

$$\log p_{S_2}^* = \Delta G_r^*/4.5756/T$$

At 500°K and 1000°K, the values of ΔG_r° and $\log p_{S_2}$ are:

$$500^\circ\text{K} \quad \Delta G_r^\circ = 2 \times (-24498) - 2 \times 0 - 11702 = -60698(\text{cal.})$$

$$E_{sse}^\circ = \frac{-60698}{92.242} = -658(\text{mv})$$

$$\log p_{S_2}^\circ = \frac{-60698}{4.5756 \times 500} = -26.5312 (\text{atm})$$

$$1000^\circ\text{K} \quad \Delta G_r^\circ = 2 \times (-23362) - 2 \times 0 - 0 = -46724(\text{cal})$$

$$E_{sse}^\circ = \frac{-46724}{92.242} = -506(\text{mv})$$

$$\log p_{S_2}^\circ = \frac{-46724}{4.5756 \times 1000} = -10.2116(\text{atm})$$

If ΔG_r° is proximately linear with T at given temperature range, one obtains a relationship as follows:

$$\Delta G_r^\circ(T) = \frac{\Delta G_r^\circ(T_2) - \Delta G_r^\circ(T_1)}{T_2 - T_1} (T - T_1) + \Delta G_r^\circ(T_1)$$

or reaction (1), from 500° to 1000°K, the approximate formulae are

$$\begin{aligned} \Delta G_r^\circ &= \frac{-46724 + 60698}{1000 - 500} (T - 500) - 60698 \\ &= -74672 + 27.948 T \end{aligned}$$

$$E_{sse}^\circ = \frac{-74672 + 27.948 T}{92.242} = -809.5 + 0.303 T$$

$$\text{and } \log p_{S_2}^\circ = \frac{-74672 + 27.948 T}{4.5756 T} = -16319.6/T + 6.108$$

4. EQUILIBRIUM DIAGRAM AND THEIR INTERPRETATION

4.1. The setting-up of the equilibrium diagrams

4.1.1. Figure 1. Vapor pressure and decomposition pressure of FeS(troilite)

In figure 1, we have drawn lines which relate to the influence of temperature on the volatilization of condensed FeS, and based on thermo-

dynamical data given in the JANAF tables⁽³⁾.

These lines relate respectively to the two following reactions:

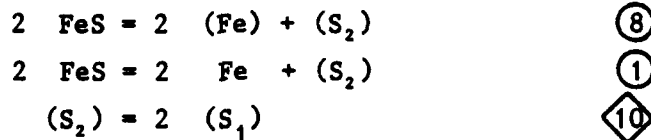
line ⑦ Volatilization of FeS with formation of gaseous (FeS) according to reaction $\text{FeS} = (\text{FeS})$ ⑦

These values of vapor p_{FeS} may be represented fairly well by the following approximate formulae:

1000 - 1463°K	$\log p_{\text{FeS}} = -23\,471/T + 8.075$
1463 - 2000°K	$-21\,041/T + 6.415$
2000 - 3500°K	$-19\,972/T + 5.880$

(see table IV page 33).

line ①' Decomposition of FeS with formation of gaseous (Fe), (S₁), (S₂) and condensed Fe (solid below 1809°K, and liquid above 1809°K) according to reactions:



These values of the decomposition pressure $P = p_{\text{Fe}} + p_{\text{S}_2} + p_{\text{S}_1}$ (which correspond to the equilibria between condensed FeS and condensed Fe) may be represented fairly well by the following approximate formulae:

1000 - 2000°K	$\log p = -15\,390/T + 5.179$
2000 - 3500°K	$= -16\,121/T + 5.545$

These two equilibrium conditions will be discussed in section 4.3 of the present report (page 14).

From figure 1 one sees that the volatilization of ferrous sulphide which occurs by heating does not result of the formation of gaseous (FeS), but its decomposition with formation of gaseous (Fe), (S₂), and (S₁). Gaseous (FeS) does not exist in appreciable amount.

4.1.2. Figures 2 and 3. Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe with consideration of the pyrrhotite of formula $FeS_{1.140}$

Figure 2 shows the equilibrium diagram for system S-Fe drawn by using the formulae given in table IV (pages 31 to 35). Figure 3 is an enlargement of part of figure 2.

4.1.3. Figures 6 to 7 and 9 to 11. Equilibrium diagram $\log p_{S_2} = f(1/T)$ and $E_{sse} = f(T)$ for the system S-Fe with consideration of pyrrhotite of different formulae

a) Equilibrium diagram based on the data given in the JANAF tables

It is likely that any solid substance which has a non stoichiometric chemical formula, such as pyrrhotite $FeS_{1.140}$ (which is sometimes written Fe_7S_8) is in fact part of a series of solid solutions, and that, thus, the solubility conditions should be considered as a whole. It would be a mistake to consider only equilibria involving one form of the series (for instance the equilibria $FeS_2/FeS_{1.140}$ and $FeS_{1.140}/FeS$, or $FeS_{1.140}/Fe$) without considering the equilibria involving the other forms of the series (for instance FeS_2/FeS_{1+X} , with different values of the non stoichiometric index $1+X$, and FeS_{1+X}/Fe).

As previously show in a study related to system O-Fe (1.4 pp.7-14), it is true notably for the wüstite $Fe_{0.947}O$, which is in fact part of series of non stoichiometric ferrous oxide $Fe_{1-X}O$, where the index $1-X$ extends from 0.95 to 0.84. This is also true for the non stoichiometric magnetite where this index extends from 0.750 to 0.726. In the diagrams which are prepared in the present work, the stability conditions of such non stoichiometric substance do not appear as a single line (relating to an univariant equilibrium), but as a surface (relating to a divariant equilibrium) which includes several lines corresponding to different stoichoimetries. Examples of this have been given in reference (1.4) (figures 14 and 15, page 17C).

b). Equilibrium diagram taking into account the work of T.ROSENQVIST (5) (figures 4 to 7)

It is well known that pyrrhotite FeS_{1+X} (which is called in German "Magnetkies") is in fact a solid solution of sulphur in ferrous sulphide FeS (4, p.345) with different stoichiometries. An outstanding experimental work on the thermodynamic behavior of iron sulphides has been published in 1954 by T.ROSENQVIST (5), this work has led to figure 4a which relates to the behavior of iron and iron sulphides in the presence of $(\text{H}_2\text{S})/(\text{H}_2)$ mixtures, in the temperature range from about 500 to 1500°C. In this figure 4a the indexes 42,39,..... till 0.01,0.005, indicate the concentrations in sulphur, in weight %.

Figure 4b shows the same diagram as figure 4a with a reverse scale for the abscissa (high temperature to the right), as is used for the diagrams drawn in our Atlases. In this figure 4b, we have converted the concentrations in sulphur (weight %) into the corresponding values of the stoichiometric index $1+X$ (relating to the formula FeS_{1+X}). This correspondance is given in the following table

S weight %	42	39	38	37	34	32	30	20
S mole per loop	1.313	1.219	1.188	1.156	1.062	1.000	0.938	0.625
Fe mole per loop	1.038	1.092	1.110	1.128	1.182	1.218	1.253	1.432
$1+X$	1.264	1.116	1.070	1.025	0.898	0.821	0.748	0.436
$\log(X \cdot 10^3)$	2.42	2.06	1.84	1.40	-	-	-	-
$\log(1+X)$	0.101	0.048	0.029	0.011	-0.047	-0.086	-0.126	-0.316

4	2	1	0.1	0.05	0.03	0.01	0.005
0.125	0.063	0.031	0.0030	0.0015	0.0009	0.0003	0.00016
1.719	1.755	1.773	1.7887	1.7896	1.7900	1.7903	1.7904
0.073	0.036	0.017	0.0016	0.0008	0.0005	0.0002	0.0001
-	-	-	-	-	-	-	-
-1.137	-1.444	-1.770	-2.796	-3.097	-3.301	-3.699	-4.000

In this figure 4b, where we have added the isobar lines for $\log p_{\text{S}_2}$, and where the two parts of figure 4a have been drawn with a single ordinate scale (without interruption between 10^0 and 10^{-1}), we have

also indicated with thicker lettering the areas of stability of the condensed substances FeS_2 , FeS_{1+X} , $\alpha, \beta, \delta\text{Fe}$. It may be seen that there is no area of stability for solid FeS (troilite). FeS is stable only along a given line. This means that any increase of the sulphur (or H_2S) content of the gaseous atmosphere leads to a sulphidation of troilite with formation of pyrrhotite, and that any decrease of this sulphur (or H_2S) content leads to a desulphidation of troilite with formation of iron (containing a slight amount of dissolved sulphur).

Figure 5 shows a still unpublished equilibrium diagram for the system S-H, which was drawn in 1940⁽⁶⁾. In this diagram, which is drawn as a function of $\log p_{\text{S}_2}$ and $1/T$, the family of lines a represents the equilibrium conditions of reaction $2(\text{H}_2) + (\text{S}_2) = 2(\text{H}_2\text{S})$ according to the following formulae, valid for the temperature ranges of 500 to 1000°K and 1000 to 2000°K,

$$\begin{aligned} 500 - 1000^\circ\text{K} \quad \log p_{\text{S}_2} &= -9250.4/T + 4.9489 + 2\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) \\ 1000 - 2000^\circ\text{K} \quad &= -9440.7/T + 5.1482 + 2\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) \end{aligned}$$

These formulae allow to draw in figure 4b isobar lines for $\log p_{\text{S}_2}$; they also allow to convert the values of $\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2})$ given in this figure 4b into $\log p_{\text{S}_2}$, and thus to draw figures 6 and 7 which represent, as a function of $\log p_{\text{S}_2}$ and $1/T$, the equilibrium diagram shown on figure 4b as a function of $\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2})$ and $1/T$. It is likely that, due to some imperfections relating to the stability of pyrrhotite FeS_{1+X} (for which the lines relating to given values of $(1+X)$ are somewhat abnormal), notably below its transformation temperature (598°K), figures 6 and 7 are not fully reliable and should be considered as provisional and subject to amendments.

c). Equilibrium diagram taking into account the work of P.TOULMIN and P.B.Jr.BARTON (7)

In 1964 using the electrometallurgical method which was developed by themselves, P.TOULMIN and P.B.Jr.BARTON determined the variation in the composition of hexagonal pyrrhotite in the condensed system as a function of sulphur fugacity and temperature. They also, according

to their experimental results, derived the following formula for the calculation of $\log f_{S_2}$ under given temperatures and mol fractions of FeS in pyrrhotite (in the system FeS-S₂)

$$\log f_{S_2} = (70.03 - 85.83N)(1000/T - 1) + 39.03\sqrt{1-0.9981N} - 11.91 \quad \text{..... (A)}$$

where f_{S_2} is the fugacity of sulphur relative to the ideal diatomic gas at 1 atm. Their results are shown in figure 8.

Figures 9 and 10 are two revised diagrams which were drawn by making use of the work of TOULMIN and BARTON. The mol fraction of FeS, N_{FeS} , has been converted into the corresponding non stoichiometric index (1+X) according to following formula:

$$N_{FeS} = \frac{2}{1 + (1 + X)}$$

If the pressure is not very high, p_{S_2} may be considered to be equal to the fugacity f_{S_2} . Thus, the following proximate formula was obtained by virtue of equation (A):

$$\log p_{S_2} = (70.03 - \frac{171.66}{1+(1+X)})(1000/T-1) + 39.30\sqrt{1 - \frac{1.9962}{1+(1+X)}} - 11.91 \quad \text{..... (B)}$$

Then, the formula for E_{sse} was obtained:

$$E_{sse} \text{ (mv)} = (3.476 - \frac{8.515}{1+(1+X)})(1000-T) + 1.949\sqrt{1 - \frac{1.9962}{1+(1+X)}} \cdot T - 0.5908T \quad \text{..... (C)}$$

By means of this formula (C) and of the formula in table IV, an equilibrium diagram $E_{sse} = f(T)$ was drawn in figure 11.

In figures 9, 10 and 11, above about 1000°K, the curves relating to non stoichiometric pyrrhotite with different indexes (1+X) were estimated according the phase diagram given in figure 12, from which one can determine the indexes 1+X corresponding to different temperatures. The dotted lines drawn in the area of stability of solid pyrrhotite have been drawn by extrapolation so

that they cross the melting curve CDE at the temperature given in the phase diagram published by J.CHIPMAN (fig.12). The isostoichiometric-lines given in figures 9, 10 and 11 in the area of stability of liquid ferrous sulphide have also been drawn according to figure 12.

In figure 10, the isobar lines for total pressure of ($p_{Fe} + p_{S_1} + p_{S_2}$) were calculated with computer, the values are listed as follows.

$\log(p_{Fe} + p_{S_1} + p_{S_2})$	$\log p_{S_2}$	T°K	1000/T
-6	-7	1596	0.6265
	-6.3010	1561	0.6401
	-6.0458	1474	0.6786
-5	-6	1729	0.5785
	-5.301	1687	0.5926
	-5.0458	1584	0.6312
-4	-5	1886	0.5301
	-4.3010	1834	0.5452
	-4.0458	1713	0.5839
-3	-4	2086	0.4794
	-3.3010	2020	0.4949
	-3.0458	1864	0.5366
-2	-3	2332	0.4288
	-2.3010	2248	0.4448
	-2.0458	2051	0.4876
-1	-2	2644	0.3783
	-1.3010	2532	0.3949
	-1.0458	2278	0.4390
0	-1	3051	0.3278
	-0.3010	2897	0.3451
	-0.0458	2559	0.3908
+1	0	3605	0.2774
	0.6990	3383	0.2956
	0.9542	2915	0.3430
+2	1	4404	0.2271
	1.6990	4060	0.2463
	1.9542	3382	0.2956

These isobar lines take on a curve, after being identical with line ⑪ as long as (S_2) predominates, they follow the lines for iron when (Fe) become largely predominant, Along any isobar curve, the total pressure of ($p_{Fe} + p_{S_1} + p_{S_2}$) is always a constant.

4.2. Metallic iron

As shown notably by figures 6,7 and 9 to 11, solid metallic iron, which is stable bellow line ①, changes from the α to the γ form at $1184^\circ K$, to the δ form at $1665^\circ K$, and becomes liquid at $1809^\circ K$. The vapor pressure of metallic iron at different temperature are listed as follows.*

$\log p_{Fe}$	-6	-5	-4	-3	-2	-1	0	+1	+2
$T^\circ K$	1604	1738	1897	2102	2354	2674	3136	3674	4518
$1000/T$.6234	.5753	.5272	.4757	.4248	.3739	.3189	.2722	.2213

Above line ①, solid α and γ Fe may be, up to about $1261^\circ K$ ($988^\circ C$), sulphidized into pyrrhotite FeS_{1+x} . Above $1261^\circ K$, the sulphidation of α or δ Fe leads to the formation of a liquid melt which contains less sulphur than the pyrrhotite (which has always more than 36.4% S). The formula of this melt is about $FeS_{0.8}$

(30% S) at $1261^\circ K$ ($988^\circ C$) and $FeS_{0.44}$ (20% S) at $1573^\circ K$ ($1300^\circ C$).

Above about $1500^\circ K$, the sulphur content of the melt becomes much smaller, $FeS_{0.07}$ (4% S) at $1670^\circ K$ and $FeS_{0.04}$ (2% S) at $1740^\circ K$.

Above $1740^\circ K$ ($1467^\circ C$), the melt is essentially liquid iron containing some sulphur in an amount which depends on the partial sulphur pressure of the gaseous atmosphere, $FeS_{0.04}$ (2% S) for $\log p_{S_2} = -5.0$ (atm), and $FeS_{0.02}$ (1% S) for $\log p_{S_2} = -5.5$ (atm).

* These values are slightly different from the values given in a previous report (1.3,p.3), because the newer μ_{Fe}° and $\mu_{(Fe)}^\circ$ were used at present work.

Solid iron may dissolve much less sulphur than the liquid melt, its higher sulphur content corresponds to $\text{FeS}_{0.0002}$ (0.01% S) at 1261°K (at $\log p_{\text{S}_2} = -7.0$) and to $\text{FeS}_{0.0005}$ (0.03% S) at 1400°K (at $\log p_{\text{S}_2} = -5.5$).

4.3. The stoichiometric ferrous oxide FeS (troilite)

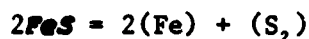
It appears from figures 6 and 9 that troilite is stable only along line ① (up to 1261°K), and does not have any area of thermodynamic stability. Above line ①, troilite is sulphurized with formation of non stoichiometric pyrrhotite FeS_{1+x} , the sulphur content of which increases with the sulphur pressure of gaseous atmosphere, at 1261°K (988°C) from slightly more than FeS (36.5% S), at $\log p_{\text{S}_2} = -7.0$ (atm), up to slightly more than $\text{FeS}_{1.27}$ (42.1% S) at $\log p_{\text{S}_2} = +1.8$ (atm). Below line ①, troilite is desulphurized with formation of metallic iron Fe containing a slight amount of sulphur, at 1261°K, $\text{FeS}_{0.0002}$ (0.01% S), at $\log p_{\text{S}_2} = -7.0$ (atm).

According to figures 6 and 9, stoichiometric FeS might be formed by cooling molten ferrous sulphide FeS_{1+x} below 1261°K under a very low sulphur pressure (10^{-7} atm), or by desulphurization of pyrrhotite FeS_{1+x} under similar conditions. And this might explain the well known fact, which we have learned from Ivan de MAGNÉE⁽⁸⁾, that troilite, which does not form lonely on the earth as a distinct mineral, is common in meteorites and lunar rocks^(9,10)*. When coming in presence of the cold interstellar vacuum, molten iron sulphides may be altogether desulphurized and quenched with formation of stoichiometric FeS.

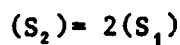
Furthermore, figures 7 and 10 show that, when heated at different temperatures, molten ferrous sulphide FeS_{1+x} will decompose till the system reaches about line ①', which relates to its decomposition with formation of metallic iron and gaseous (S_2), (S_1) and (Fe), according to the following reactions (which relate

* troilite is always associated with pyrrhotite

to the decomposition of stoichiometric FeS :



and



As show at page 7 and in figure 1, the equilibrium conditions of this high temperature decomposition of molten ferrous sulphide may be expressed approximately by the following relations where

$$P = p_{\text{S}_2} + p_{\text{S}_1} + p_{\text{Fe}}$$

$$1000 - 2000^\circ\text{K}$$

$$\log P = -15\,390/T + 5.179$$

$$2000 - 3500^\circ\text{K}$$

$$= -16\,121/T + 5.545$$

These formulae lead to the following approximate values for the influence of temperature on the decomposition pressure of molten ferrous sulphide

log P(atm)	-6	-5	-4	-3	-2	-1	0	+1	+2
T°K	1377	1512	1677	1882	2137	2463	2907	3547	4548
1000/T	.7264	.6614	.5964	.5315	.4680	.4060	.3439	.2819	.2199

4.4. The non stoichiometric ferrous oxide FeS_{1+x} (pyrrhotite)

The mineral pyrrhotite is often considered as Fe_7S_8 (or $\text{Fe}_{0.875}\text{S}$ or $\text{FeS}_{1.140}$), but may, as show by T.ROSENQVIST⁽⁵⁾, have different compositions ranging from less than 37% S till more than 42% S. This corresponds, as shown by figures 6,7 and 9 to 11 of the present paper, to a series of solid solutions ranging from less than $\text{FeS}_{1.025}$ to more than $\text{FeS}_{1.264}$. In fact, pyrrhotite is , as said in page 8 a solid solution of sulphur in FeS .

According to figures 6,7,9 to 11, any decrease of the sulphur pressure below line ① (which corresponds to the equilibrium between stoichiometric FeS (troilite) and metallic iron) will lead to a desulphurizations of pyrrhotite with formation of iron. On the right

side of line CDE (i.e. when heated above about 1210 to 1463°K depending on the sulphur pressure), pyrrhotite will melt with formation of liquid FeS_{1+X} whose stoichiometry will depend on this sulphur pressure. For example (see figure 10, page 42), at about 1450°K the substances which are in equilibrium with each other are solid $\text{FeS}_{1.06}$ and liquid $\text{FeS}_{1.00}$. At other temperatures, the compositions will be different. At about 1463°K (point D) both liquid and solid have the same composition $\text{FeS}_{1.07}$. Above point D the index values for the liquid are higher than for the solid. On the contrary, below point D, the $1+X$ values for the liquid are smaller than for the solid. At higher temperatures, the equilibrium pressures of (S_2), (S_1) and (Fe) of liquid pyrrhotite increase, and pyrrhotite may thus decompose with formation of these three gases. The exact values of $\log p_{\text{S}_2}$ and $\log p_{\text{S}_1}$ are given by the isobars ⑪ and ⑩. But the exact isobars for $\log p_{\text{Fe}}$ have not been drawn, due to the lack of reliable information relating to the composition of liquid FeS_{1+X} . Tentatively, we have drawn on figure 10, the family of straight plain lines ⑧ which would correspond to given equilibrium values of $\log p_{\text{Fe}}$ in the hypothetical presence of stoichiometric FeS ; we have also drawn a family of slightly in curved dotted lines which would probably correspond better to the equilibrium values of $\log p_{\text{Fe}}$ in the real presence of non-stoichiometric FeS_{1+X} , such provisional isobar lines might perhaps be improved in the future.

It seems that the chemical behavior of pyrrhotite is very complicate and still largely unknown; we shall content ourselves to mention that, as shown by figures 2,6 and 9 to 11, there are two forms of hexagonal pyrrhotite (low temperature β and high temperature γ) whose equilibrium temperature is 598°K (325°C). Above line (5), pyrrhotite may be transformed into pyrite FeS_2 .

4.5. Ferric sulphide FeS_2 , (pyrite)

Two polymorphs of FeS_2 are known; pyrite and marcasite. The latter is known to be metastable with respect to the pyrite at all temperatures. For this reason we did not consider marcasite in the present work.

Figure 9 shows that FeS_2 is stable above line (5). Line (2), which shows the conditions of the stability of condensed sulphur, is a limitation for the equilibrium diagrams of all sulphur containing systems. Beyond line (2), all the sulphur existing in the gas phase may be converted into solid or liquid elementary sulphur. No stable equilibrium can be located at any point which is above line (2).

If heated at different sulphur pressures, pyrite FeS_2 will decompose into solid or liquid pyrrhotite FeS_{1+x} . The decomposition temperatures at several given sulphur pressures are listed in table V.

log p _{S₂}	formation of solid FeS _{1+X}		formation of liquid FeS _{1+X}	
	T°K	T°C	T°K	T°C
-6	730	457	1315	1042
-5	760	487	1360	1087
-4	790	517	1400	1127
-3	830	557	1430	1157
-2	875	602	1449	1176
-1	925	652	1464	1191
0	975	702	1460	1187
+1			1410	1137

Table V. Temperatures of dissociation of pyrite FeS₂ with formation of different iron sulphides, under different pressures in gaseous sulphur.

4.6. Equilibrium diagram for the S-Fe system of the SZ = f(T) type

Figures 12a and 12b give, for memory, the very well known sulphur-iron diagrams drawn after John CHIPMAN⁽¹¹⁾ and L.A.TAYLOR⁽¹²⁾.

Figure 13 is a modified presentation of figure 12a. Isobar lines were added. Also included in this diagram are all the triple points (A to C and E to H) and the maximum melting temperature of high temperature hexagonal pyrrhotite (γ FeS_{1+X}) (point D). All these points were already plotted in the equilibrium diagrams given at figures 6,7 and 9 to 11. At the top of figure 13, a non-linear scale of the values of 1+X is given.

Comparing figure 13 with figures 6,7 and 9 to 11, it is noticed that the "empty spaces" existing at figure 13 between the solidus and the liquidus lines, or between the different solidus lines, do not exist in figures 6,7 and 9 to 11. These "empty spaces" do not correspond to any "real" state. In figure 13, only pyrrhotite (FeS_{1+X}) has an area of stability which has been shown by the shaded

area. In this figure 13, the points B_1, B_2 and B_3 correspond in fact to one and the same equilibrium solid FeS_2 /liquid S /solid γFeS_{1+x} , which is indicated by one point B in diagrams of $\log p_{\text{S}_2} = f(1/T)$ or $E_{\text{sse}} = f(T)$ type: Point C_1, C_2 and C_3 of figure 13 correspond to one and the same equilibrium liquid S or gaseous sulphur/liquid FeS_{1+x} /solid γFeS_{1+x} shown by the point C, in figures 6, 7 and 9 to 11. There is some disagreement in the temperatures given for points C in figure 13 (1356°K) and in figure 11 (about 1210°K). Using the same method, one sees that, points E_1, E_2, E_3 of figure 13 stand for the equilibrium solid γFe / liquid FeS_{1+x} / solid γFeS_{1+x} and correspond to point E of figure 11; points F_1 and F_2 of figure 13 are shown as one point F in figure 11 and is the triple point for the equilibrium solid αFe / solid γFe / solid γFeS . In all these figures, line AG separates the stable areas of βFeS_{1+x} (low temperature hexagonal pyrrhotite) and γFeS_{1+x} (high temperature hexagonal pyrrhotite) and points G and A are two triple points for the equilibria solid γFeS / solid βFeS / solid αFe and solid αFeS_{1+x} / solid βFeS_{1+x} / solid FeS_2 (pyrite) respectively.

Due to the complication of the S-Fe system and to lack of information, we could not show the equilibrium conditions at low temperatures (below about 500°K), and we have put some question-marks on this area. This diagram might be revised as a result of further work.

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	CONDENSED SUBSTANCES						GASEOUS SUBSTANCES			
	A	B	C	D ₁	D ₂	E	F	G	H	I
T°K	S	FE	FES	FE0.877S	FES1.140	FES2	(S1)	(S2)	(FE)	(FES)
0	0	0	-24421	-23412	-28976	-40121	65663	30636	98740	88401
100	0	0	-24371	-23405	-28968	-39848	62885	26980	95588	84083
200	0	0	-24356	-23450	-29019	-39120	59706	22923	91978	79331
298	0	0	-24368	-23541	-29123	-38256	56333	19027	88393	74723
300	0	0	-24368	-23543	-29123	-38239	56473	18955	88323	74637
400	0	0	-24400	-23659	-29258	-37246	53251	15131	84668	70036
500	0	0	-24498	-23667	-29267	-35900	50189	11702	81021	65657
600	0	0	-24630	-23664	-29263	-34387	47205	8479	77396	61412
700	0	0	-24780	-23677	-29278	-32769	44268	5387	73804	57270
800	-1198	0	-26103	-26863	-30631	-33466	40171	0	70248	52023
900	258	0	-24737	-25359	-28916	-28782	38757	0	66736	49524
1000	1678	0	-23362	-23846	-27910	-24101	37334	0	63279	47083
1100	3067	0	-21950	-22295	-25422	-19392	35904	0	59898	44728
1200	4428	0	-20523	-20733	-23641	-14680	34469	0	56578	42434
1300	5763	0	-19096	-19172	-21861	-9977	33028	0	53303	40189
1400	7076	0	-17693	-17635	-20108	-5302	31585	0	50052	37972
1500	8368	0	-16508	-16128	-18390		30137	0	46823	35781
1600		0	-15662	-14635	-16710		28687	0	43617	33617
1700		0	-14820	-13218	-15072		27234	0	40438	31485
1800		0	-13971	-11816	-13473		25779	0	37293	29393
1900		0	-12938				24323	0	34341	27517
2000		0	-11888				22865	0	31435	25688
2500		0	-6595				15554	0	17284	16990
3000		0	-1230				8217	0	3647	8936
3500		9593	13554				856	0	0	10773
4000							-6527	0	0	16664
4500							-13931	0	0	22714
5000							-21354	0	0	28925
5500							-28791	0	0	35294
6000							-36239	0	0	41820
368	0							16304		
388	0							15545		
718	-2426							0		
1314	6136							0		

TABLE I Standard chemical potentials μ° (or standard enthalpies of formation ΔG_f°) of the considered substances (calories.mole⁻¹).

Equilibria	Reactions	ΔG° (calories per mole group)	Equilibrium	Formulae
SULFUR SYSTEM				
<u>Reaction involving one condensed substance</u>				
②	$S \rightleftharpoons (S_2) = 2 S$	$= 2 \mu_S^\circ - \mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ$	
<u>Reactions involving one gaseous substance</u>				
⑩	$(S_1) \rightleftharpoons (S_2) = 2 (S_1)$	$= 2 \mu_{(S_1)}^\circ - \mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 9.1512 T \log p_{S_1}$	
⑪	$(S_2) \rightleftharpoons (S_2)$	$= 0$	$RT \ln p_{S_2} = -4.5756 T \log p_{S_2}$	
⑬	$(S_1)/(S_2) \rightleftharpoons 2 (S_1) + (S_2) = 2 (S_2)$	$= \mu_{(S_2)}^\circ - \mu_{(S_1)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 9.1512 T \log(p_{S_2}/p_{S_1})$	
IRON SYSTEM				
<u>Reaction involving one condensed substance</u>				
⑧	$Fe/(Fe) \rightleftharpoons Fe = (Fe)$	$= \mu_{(Fe)}^\circ - \mu_{Fe}^\circ$	$\log p_{Fe} = -\Delta G^\circ / 4.5756 T$	
SULFUR-IRON SYSTEM				
<u>Reactions involving two condensed substances</u>				
①	$Fe/FeS \rightleftharpoons 2 Fe + (S_2) = 2 FeS$	$= 2 \mu_{Fe}^\circ - \mu_{(S_2)}^\circ - 2 \mu_{FeS}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ$	
②	$Fe/FeS_{1.140} \rightleftharpoons 1.734Fe + (S_2) = 1.734FeS_{1.140}$	$= 1.734\mu_{Fe}^\circ - \mu_{(S_2)}^\circ - 1.734\mu_{FeS_{1.140}}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ$	
③	$FeS/FeS_{1.140} \rightleftharpoons 14.285FeS + (S_2) = 14.285FeS_{1.140}$	$= 14.285\mu_{FeS}^\circ - \mu_{(S_2)}^\circ - 14.285\mu_{FeS_{1.140}}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ$	
④	$FeS_{1.140}/FeS \rightleftharpoons 2.326FeS_{1.140} + (S_2) = 2.326FeS_2$	$= 2.326\mu_{FeS_{1.140}}^\circ - \mu_{(S_2)}^\circ - 2.326\mu_{FeS_2}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ$	
⑤	$FeS_{1.140}/FeS_2 \rightleftharpoons \frac{2}{1.140}FeS_{1.140} + (S_2) = \frac{2}{1.140}FeS_2$			
<u>Reactions involving 1 condensed substance and 1 gaseous substance</u>				
⑥	$Fe/(FeS) \rightleftharpoons 2 Fe + (S_2) = 2 (FeS)$	$= 2 \mu_{(FeS)}^\circ - \mu_{(S_2)}^\circ - 2 \mu_{Fe}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 9.1512 T \log p_{FeS}$	
⑦	$FeS/(FeS) \rightleftharpoons FeS = (FeS)$	$= \mu_{(FeS)}^\circ - \mu_{FeS}^\circ$	$\log p_{FeS} = -\Delta G^\circ / 4.5756 T$	
⑧	$(Fe)/(FeS) \rightleftharpoons 2 (Fe) + (S_2) = 2 FeS$	$= 2 \mu_{Fe}^\circ - \mu_{(S_2)}^\circ - 2 \mu_{(FeS)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ - 9.1512 T \log p_{Fe}$	
⑨	$(Fe)/(FeS_{1.140}) \rightleftharpoons 1.734(Fe) + (S_2) = 1.734FeS_{1.140}$	$= 1.734\mu_{Fe}^\circ - \mu_{(S_2)}^\circ - 1.734\mu_{(FeS_{1.140})}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ - 8.0256 T \log p_{Fe}$	
<u>Reaction involving 2 gaseous substances</u>				
⑩	$(Fe)/(FeS) \rightleftharpoons 2 (Fe) + (S_2) = 2 (FeS)$	$= 2 \mu_{(FeS)}^\circ - \mu_{(S_2)}^\circ - 2 \mu_{(Fe)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 9.1512 T \log(p_{FeS}/p_{Fe})$	
<u>Reaction involving 1 condensed substance and 2 gaseous substances</u>				
⑪	$(Fe)/(S_2), Fe \rightleftharpoons (Fe) + (S_2) = Fe + (S_2)$	$= \mu_{Fe}^\circ - \mu_{(Fe)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 4.5756 T \log(p_{S_2}/p_{Fe})$	
⑫	$(Fe)/(S_1), Fe \rightleftharpoons 2 (Fe) + (S_2) = 2 Fe + 2(S_1)$	$= 2 \mu_{Fe}^\circ + 2\mu_{(S_1)}^\circ - 2 \mu_{(Fe)}^\circ - \mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 9.1512 T \log(p_{S_1}/p_{Fe})$	
⑬	$(Fe)/(S_2), FeS \rightleftharpoons 2/3 (Fe) + (S_2) = 2/3 FeS + 2/3(S_2)$	$= 2/3 \mu_{FeS}^\circ - 2/3 \mu_{(Fe)}^\circ - 1/3 \mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 3.0504 T \log(p_{S_2}/p_{Fe})$	
⑭	$(Fe)/(S_2), FeS_{1.140} \rightleftharpoons 0.637(Fe) + (S_2) = 0.637FeS_{1.140} + 0.637(S_2)$	$= 0.637\mu_{FeS_{1.140}}^\circ - 0.637\mu_{(Fe)}^\circ - 0.363\mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 2.9147 T \log(p_{S_2}/p_{Fe})$	
⑮	$(Fe)/(S_1), FeS \rightleftharpoons (Fe) + (S_2) = FeS + (S_1)$	$= \mu_{FeS}^\circ + \mu_{(S_1)}^\circ - \mu_{(Fe)}^\circ - \mu_{(S_2)}^\circ$	$RT \ln p_{S_2} = -\Delta G^\circ + 4.5756 T \log(p_{S_1}/p_{Fe})$	

TABLE II Equilibria and reactions considered
Formulae for the calculation of the standard free
enthalpies of reaction ΔG°

(see page 5)

		①			②			③		
		PE / PEB			PE / PEBL 140			PEB / PEBL 140		
T°K	1000/T	$\Delta G_f^{\circ}(\text{CAL})$	$E_{298}^{\circ}(\text{mV})$	$\text{LOG } P_{S_2}$	$\Delta G_f^{\circ}(\text{CAL})$	$E_{298}^{\circ}(\text{mV})$	$\text{LOG } P_{S_2}$	$\Delta G_f^{\circ}(\text{CAL})$	$E_{298}^{\circ}(\text{mV})$	$\text{LOG } P_{S_2}$
0	∞	-79478	-861	-88	-81497	-883	-88	-97704	-1037	-88
100	10.000	-79732	-880	-143.4409	-77787	-843	-178.0883	-92448	-1004	-882.4887
200	5.000	-71638	-776	-78.2794	-73888	-809	-88.6498	-87933	-970	-87.8874
298	3.364	-67763	-734	-49.6468	-70108	-768	-81.4166	-84788	-948	-62.7698
300	3.333	-67691	-733	-49.3130	-70048	-767	-81.0843	-84708	-948	-63.3186
400	2.500	-63931	-693	-34.9384	-66447	-728	-34.3048	-80887	-916	-64.1886
500	2.000	-60498	-658	-24.9312	-63036	-683	-27.8831	-77887	-883	-34.8788
600	1.667	-57739	-628	-21.0319	-59886	-648	-21.7844	-74861	-859	-27.1928
700	1.429	-54767	-598	-17.1383	-56748	-613	-17.7191	-71848	-834	-21.7487
800	1.250	-51896	-568	-14.2621	-53786	-588	-14.6773	-68888	-801	-17.6784
900	1.111	-49474	-538	-12.0148	-50718	-569	-12.3161	-65977	-847	-14.8968
1000	1.000	-46784	-506	-10.2116	-48794	-538	-10.4989	-63968	-794	-14.1988
1100	.909	-43988	-479	-8.7888	-46986	-503	-8.8878	-61977	-837	-9.8848
1200	.833	-41046	-444	-7.4788	-44466	-469	-7.3888	-59848	-888	-8.1119
1300	.769	-38192	-414	-6.4887	-42344	-418	-6.4462	-57698	-888	-6.4462
1400	.714	-35386	-383	-5.7848	-40547	-388	-5.3888	-55478	-873	-5.3884
1500	.667	-33016	-357	-4.8164	-38886	-349	-4.6977	-53884	-891	-3.9170
1600	.625	-31284	-339	-4.2787	-37307	-317	-4.0884	-51978	-148	-2.8448
1700	.588	-29640	-321	-3.8188	-35826	-286	-3.3986	-50999	-39	-4.687
1800	.556	-27948	-302	-3.3786	-34431	-256	-2.8878	7113	77	8436
1900	.529	-26876	-288	-2.9764						
2000	.500	-25776	-257	-2.5981						
2500	.400	-12190	-148	-1.1331						
3000	.333	-8460	-34	-1.1798						
3500	.286	7922	88	.4947						

		④			⑤			⑦	
		PEBL 140 / PEB			PE / (PEB)			PEB / (PES)	
T°K	1000/T	$\Delta G_f^{\circ}(\text{CAL})$	$E_{298}^{\circ}(\text{mV})$	$\text{LOG } P_{S_2}$	$\Delta G_f^{\circ}(\text{CAL})$	$E_{298}^{\circ}(\text{mV})$	$\text{LOG } P_{S_2}$	$\Delta G_f^{\circ}(\text{CAL})$	$\text{LOG } P_{S_2}$
0	∞	-86889	-813	-88	146166	1384	∞	112822	-88
100	10.000	-88886	-866	-114.2714	141186	1330	388.3488	108484	-837.0868
200	5.000	-66417	-802	-88.7283	138737	1471	148.3898	103487	-113.3943
298	3.364	-40870	-636	-89.3337	130319	1413	98.6481	99091	-72.6788
300	3.333	-40134	-638	-89.8383	130319	1412	94.9376	99009	-72.1283
400	2.500	-33711	-366	-18.4189	189941	1384	68.2648	94436	-51.5976
500	2.000	-27130	-294	-11.8886	119612	1296	32.2883	90138	-39.4049
600	1.667	-20377	-221	-7.4896	114348	1239	41.6383	86042	-31.3409
700	1.429	-13807	-146	-4.2171	109133	1183	34.0798	82080	-23.4172
800	1.250	-8894	-71	-1.8814	104046	1127	28.4841	78126	-21.3431
900	1.111	311	3	.0788	99048	1073	24.0388	74261	-18.0331
1000	1.000	8889	96	1.7361	94166	1020	20.3880	70448	-15.3988
1100	.909	14025	188	2.7868	89486	969	17.7728	66678	-13.2477
1200	.833	20843	288	3.7968	84846	920	15.4866	62937	-11.4661
1300	.769	27648	399	4.6471	80378	871	13.3188	59289	-9.9667
1400	.714	34438	373	5.3768	75944	823	11.8884	55643	-8.6897
1500	.667				71548	775	10.4866	52299	-7.6188
1600	.625				67234	728	9.1888	49279	-6.7312
1700	.588				62970	682	8.0984	46303	-5.9889
1800	.556				58786	637	7.1376	43364	-5.2631
1900	.529				54834	596	6.3284	40435	-4.6334
2000	.500				51376	556	5.6161	37576	-4.1061
2500	.400				33980	368	2.9788	33583	-2.0618
3000	.333				17872	193	1.3088	10164	-7.406
3500	.286				2360	28	.1474	-2781	1737

TABLE III Standard free enthalpies ΔG_f° of the considered reactions and the corresponding logarithms of partial pressures of gaseous (S_2) in equilibrium. Reactions 1 to 7

		⑧			⑨			⑩		
		(Fe) / FeS			(Fe) / FeS _{0.999}			(Fe) / (FeS)		
T°K	1000/T	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$
0	∞	-274438	-3002	-∞	-234642	-2760	-∞	-81314	-886	-∞
100	10 000	-266898	-2893	-383.3071	-245644	-2660	-326.4193	-8998	-841	-109.2834
200	5 000	-255990	-2770	-279.3967	-235146	-2549	-236.9868	-8816	-822	-92.6882
298	3 336	-244348	-2651	-179.3493	-225148	-2440	-165.1194	-8636	-802	-74.0844
300	3 333	-244340	-2640	-178.0022	-224997	-2438	-163.8816	-8630	-802	-73.7915
400	2 500	-233266	-2530	-127.4310	-214982	-2330	-117.4447	-84394	-881	-24.2988
500	2 000	-222740	-2414	-97.3599	-205144	-2223	-89.6687	-82430	-439	-18.9462
600	1 667	-212530	-2304	-77.4143	-195386	-2120	-71.2319	-80446	-438	-14.7385
700	1 429	-202554	-2195	-63.2484	-186190	-2018	-58.1313	-78434	-416	-12.0099
800	1 250	-192702	-2087	-52.6439	-176941	-1918	-48.3388	-76480	-398	-9.9877
900	1 111	-182946	-1980	-44.4259	-167773	-1818	-40.7410	-74484	-373	-8.3893
1000	1 000	-173282	-1876	-37.8709	-159948	-1723	-34.9861	-72592	-351	-7.0793
1100	909	-163696	-1774	-32.3225	-149681	-1622	-29.7330	-70340	-328	-6.0280
1200	833	-154202	-1671	-28.0841	-140704	-1528	-25.6298	-68288	-306	-5.1830
1300	769	-144798	-1569	-24.3438	-131837	-1439	-22.1639	-66228	-284	-4.4093
1400	714	-135490	-1468	-21.1810	-123060	-1334	-19.3106	-64160	-261	-3.7716
1500	667	-126662	-1373	-18.4547	-114383	-1240	-16.6684	-62084	-239	-3.2176
1600	625	-118338	-1280	-16.1943	-106813	-1147	-14.4834	-60000	-216	-2.7319
1700	588	-110516	-1198	-14.2078	-99364	-1088	-12.8170	-57906	-194	-2.3080
1800	556	-103238	-1111	-12.4486	-92043	-968	-10.8113	-55800	-171	-1.9184
1900	526	-96438	-1025	-10.8767	-84848	-894	-8.8448	-53688	-147	-1.5699
2000	500	-90046	-939	-9.4683	-77848	-818	-7.0684	-51566	-124	-1.2560
2300	435	-67738	-517	-4.1730	-54738	-517	-4.1730	-388	-6	-0.914
3000	333	-9734	-100	-7106	-9734	-100	-7106	10878	114	7706
3500	286	27108	270	1.6927	27108	270	1.6927	31946	233	1.3484
4000	250							33388	361	1.8210
4500	222							48488	492	2.3063
5000	200							57880	627	2.8886
5500	182							70888	768	3.5849
6000	167							88400	906	4.4066

		⑪			⑫			⑬		
		(Fe) / (S ₂), P _S			(Fe) / (S ₂), P _S			(Fe) / (S ₂), P _S		
T°K	1000/T	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$	$\Delta G^\circ_{\text{CAL}}$	$E_{\text{Fe}}(\text{MV})$	$\text{LOG } P_{\text{Fe}}$
0	∞	-98740	-1070	-∞	-96790	-1049	-∞	-92319	-1000	-∞
100	10 000	-93888	-1036	-208.9081	-92386	-1001	-201.9181	-88968	-964	-194.4338
200	5 000	-91978	-977	-100.3092	-87468	-948	-99.8809	-86196	-923	-92.0988
298	3 336	-88373	-928	-64.8266	-82748	-897	-60.6867	-81519	-883	-69.7884
300	3 333	-88323	-927	-64.3449	-82660	-896	-60.2188	-81446	-882	-69.3336
400	2 500	-84668	-870	-46.2606	-77966	-840	-42.0988	-77788	-842	-48.4838
500	2 000	-81021	-820	-39.4164	-73366	-796	-35.0684	-74246	-804	-38.4838
600	1 667	-77396	-829	-32.1716	-68868	-746	-28.0830	-70843	-768	-28.8846
700	1 429	-73804	-800	-23.0437	-64460	-698	-20.1284	-67317	-721	-21.0798
800	1 250	-70248	-761	-19.1909	-60194	-662	-16.4334	-64220	-696	-17.9477
900	1 111	-66736	-723	-16.2038	-56988	-626	-13.3888	-60781	-661	-14.8883
1000	1 000	-63279	-686	-13.8297	-53890	-582	-11.3406	-57766	-626	-12.6230
1100	909	-59898	-649	-11.9007	-50988	-540	-9.3044	-54866	-591	-10.8411
1200	833	-56578	-611	-10.3843	-48218	-499	-8.0822	-51400	-567	-9.3612
1300	769	-53303	-573	-8.9611	-45680	-459	-6.8171	-48866	-523	-8.1141
1400	714	-50032	-541	-7.8123	-43294	-420	-5.7687	-46163	-489	-7.0803
1500	667	-46823	-507	-6.8221	-40972	-381	-4.8623	-43830	-457	-6.1819
1600	625	-43617	-472	-5.9378	-38860	-382	-4.0787	-41819	-428	-5.3981
1700	588	-40438	-438	-5.1987	-36868	-366	-3.3990	-39838	-399	-4.7399
1800	556	-37293	-404	-4.5280	-35088	-349	-2.7960	-38179	-370	-4.1494
1900	526	-34261	-372	-3.9301	-33436	-317	-2.3047	-36619	-341	-3.6899
2000	500	-31439	-340	-3.4391	-31940	-288	-1.8730	-35281	-313	-3.1860
2300	435	-17284	-107	-1.2110	-2660	-27	-3.3889	-18919	-172	-1.3916
3000	333	-2647	-79	-2637	9160	99	6699	-3231	-38	-2366
3500	286	9993	100	5990	20978	226	1.3849	9039	97	2642

TABLE III Standard free enthalpies ΔG° of the considered reactions and the corresponding logarithms of partial pressures of gaseous (S₂) in equilibrium. Reactions 8 to 13

		(14)			(15)		
		(FE) / (S ₂), FeS _{1.140}			(FE) / (S ₂), FeS		
T°K	1000/T	ΔG _r ^o (CAL.)	E ₃₃₂ ^o (MV)	LOG P _{S₂}	ΔG _r ^o (CAL.)	E ₃₃₂ ^o (MV)	LOG P _{S₂}
0	∞	-92478	-1002	-∞	-88134	-955	-∞
100	10.000	-89137	-966	-194.8094	-84054	-911	-183.7005
200	5.000	-85398	-925	-93.3189	-79551	-862	-86.9296
298	3.356	-81765	-886	-59.9657	-75255	-815	-55.1914
300	3.333	-81697	-885	-59.5164	-75175	-814	-54.7651
400	2.500	-78064	-846	-42.6523	-70948	-769	-38.7643
500	2.000	-74502	-807	-32.5649	-67032	-726	-29.2998
600	1.667	-71020	-769	-25.8691	-63300	-686	-23.0571
700	1.429	-67618	-733	-21.1114	-59703	-647	-18.6402
800	1.250	-64259	-696	-17.5548	-56180	-609	-15.3477
900	1.111	-60930	-660	-14.7959	-52716	-571	-12.8012
1000	1.000	-58067	-627	-12.6949	-49307	-534	-10.7761
1100	.909	-54348	-589	-10.7980	-45944	-498	-9.1283
1200	.833	-51099	-553	-9.3064	-42632	-462	-7.7644
1300	.769	-47879	-519	-8.0492	-39371	-426	-6.6189
1400	.714	-44691	-484	-6.9766	-36160	-392	-5.6448
1500	.667	-41540	-450	-6.0524	-33194	-359	-4.8364
1600	.625	-38428	-416	-5.2490	-30592	-331	-4.1787
1700	.588	-35359	-383	-4.5457	-28024	-303	-3.6027
1800	.556	-32337	-350	-3.9263	-25485	-276	-3.0943
1900	.526				-22956	-248	-2.6406
2000	.500				-20458	-221	-2.2356
2500	.400				-8325	-90	-.7278
3000	.333				3340	36	.2433
3500	.286				14410	156	.8998
4000	.250						
4500	.222						
5000	.200						
5500	.182						

TABLE III Standard free enthalpies ΔG_r^o of the considered reactions
and the corresponding logarithms of partial pressures of gaseous (S₂)
in equilibrium. Reactions 14 and 15

(see page 5)

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N°	Equilibria	Temperature range (°K)	RT ln P_{S_2} (calories) ²	E_{sse} (mv)	log P_{S_2}
SYSTEM SULPHUR-IRON					
①	FE / FES	0 - 100	-79478 + 37.560 T	-861.6 + 407 T	-17370.0/T + 8.209
		100 - 200	-79810 + 40.880 T	-863.2 + 443 T	-17442.5/T + 8.934
		200 - 298	-79536 + 39.510 T	-862.3 + 428 T	-17382.6/T + 8.635
		298 - 500	-78183 + 34.970 T	-847.6 + 379 T	-17086.9/T + 7.643
		500 - 1000	-74672 + 27.948 T	-809.5 + 303 T	-16319.6/T + 6.108
		1000 - 1463	-75069 + 28.345 T	-813.8 + 307 T	-16406.4/T + 6.195
		1463 - 1809	-58164 + 16.790 T	-630.6 + 182 T	-12711.8/T + 3.669
		1809 - 2000	-63816 + 21.020 T	-713.5 + 228 T	-14384.1/T + 4.394
②	FE / FES1.140	0 - 100	-81452 + 36.700 T	-883.0 + 398 T	-17801.4/T + 8.021
		100 - 200	-81747 + 39.650 T	-886.2 + 430 T	-17845.9/T + 8.466
		200 - 298	-81396 + 37.898 T	-882.4 + 411 T	-17789.1/T + 8.283
		298 - 500	-80533 + 35.000 T	-873.1 + 379 T	-17600.5/T + 7.649
		500 - 1000	-77112 + 28.158 T	-836.0 + 305 T	-16852.9/T + 6.154
		1000 - 1809	-80607 + 31.634 T	-873.9 + 343 T	-17616.7/T + 6.918
③	FES / FES1.140	0 - 100	-93695 + 30.370 T	-1037.4 + 331 T	-20914.2/T + 6.581
		100 - 200	-95738 + 31.000 T	-1037.9 + 336 T	-20923.6/T + 6.775
		200 - 298	-94815 + 26.388 T	-1027.9 + 286 T	-20721.9/T + 5.767
		298 - 500	-97467 + 35.287 T	-1096.6 + 383 T	-21301.5/T + 7.712
		500 - 1000	-94680 + 29.712 T	-1026.4 + 322 T	-20692.4/T + 6.494
		1000 - 1463	-141142 + 76.175 T	-1530.1 + 826 T	-30846.7/T + 16.648
		1463 - 1800	-189508 + 109.234 T	-2034.5 + 1184 T	-41417.1/T + 23.873
④	FES1.140 / FES2	0 - 100	-56565 + 42.720 T	-613.2 + 463 T	-12362.3/T + 9.336
		100 - 200	-58164 + 58.710 T	-630.6 + 636 T	-12711.8/T + 12.831
		200 - 298	-58968 + 62.735 T	-639.3 + 680 T	-12887.5/T + 13.711
		298 - 500	-59661 + 65.059 T	-646.8 + 705 T	-13038.9/T + 14.219
		500 - 1000	-63123 + 71.982 T	-684.3 + 780 T	-13795.6/T + 15.732
		1000 - 1400	-55088 + 63.948 T	-597.2 + 693 T	-12039.5/T + 13.976

TABLE IV Influence of temperature on the equilibrium conditions of the considered reactions.

Approximate formulae.

IV.1 Reactions 1 to 4

(see page 5)

N°	Equilibria	Temperature range (°K)	Equilibrium	Formulae
⑥	FE / (FES)	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 1809 1809 - 2000 2000 - 3500	146166 - 49.800 T + 146632 - 54.460 T + 146597 - 54.286 T + 146364 - 53.505 T + 145058 - 50.892 T + 138390 - 44.225 T + 124799 - 36.712 T + 116730 - 32.677 T +	9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES) 9.151 T LOG P(FES)
⑦	FES / (FES)	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 1463 1463 - 2000 2000 - 3500	112822 - 43.680 T 113221 - 47.670 T 113066 - 46.998 T 112273 - 44.238 T 109865 - 39.420 T 107395 - 36.950 T 96276 - 29.350 T 91385 - 26.905 T	
⑧	(FE) / FES	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 1463 1463 - 2000 2000 - 3500	-276958 + 100.600 T - -278206 + 113.080 T - -278124 + 112.673 T - -276720 + 107.960 T - -272198 + 98.916 T - -267762 + 94.480 T - -244391 + 79.873 T - -238318 + 75.836 T -	9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE) 9.151 T LOG P(FE)
⑨	(FE) / FESL 146	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 1800	-254642 + 91.980 T - -255742 + 102.980 T - -255556 + 102.051 T - -254651 + 99.015 T - -250343 + 90.398 T - -248572 + 88.627 T -	8.026 T LOG P(FE) 8.026 T LOG P(FE) 8.026 T LOG P(FE) 8.026 T LOG P(FE) 8.026 T LOG P(FE) 8.026 T LOG P(FE)
⑩	(FE) / (FES)	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 2000 2000 - 3500	-51314 + 13.240 T + -51764 + 17.740 T + -51991 + 18.878 T + -52172 + 19.485 T + -52468 + 20.076 T + -53290 + 20.898 T + -57723 + 23.115 T +	9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE)) 9.151 T LOG(P(FES)/P(FE))

TABLE IV Influence of temperature on the equilibrium conditions of the considered reactions.

Approximate formulae.

IV.2 Reactions 6 to 10

(see page 5)

$E_{sse} (mv) (= \frac{RT \ln p_{S_2}}{92.242})$			$\log p_{S_2} (= \frac{RT \ln p_{S_2}}{4.5756 T}) \text{ (or } \log p)$		
1584.6 -	540 T +	.099 T LOG P(FES)	31944.7/T -	10.884 +	2.000 LOG P(FES)
1589.6 -	590 T +	.099 T LOG P(FES)	32046.5/T -	11.902 +	2.000 LOG P(FES)
1599.3 -	589 T +	.099 T LOG P(FES)	32038.9/T -	11.864 +	2.000 LOG P(FES)
1586.7 -	580 T +	.099 T LOG P(FES)	31987.9/T -	11.694 +	2.000 LOG P(FES)
1572.6 -	552 T +	.099 T LOG P(FES)	31702.5/T -	11.122 +	2.000 LOG P(FES)
1500.3 -	479 T +	.099 T LOG P(FES)	30245.2/T -	9.665 +	2.000 LOG P(FES)
1353.0 -	398 T +	.099 T LOG P(FES)	27274.9/T -	8.023 +	2.000 LOG P(FES)
1265.5 -	354 T +	.099 T LOG P(FES)	25511.4/T -	7.142 +	2.000 LOG P(FES)
			LOG P(FES) = -24657.3/T +	9.546	
			LOG P(FES) = -24744.5/T +	10.418	
			LOG P(FES) = -24710.6/T +	10.250	
			LOG P(FES) = -24337.3/T +	9.668	
			LOG P(FES) = -24011.1/T +	8.615	
			LOG P(FES) = -23471.2/T +	8.075	
			LOG P(FES) = -21041.2/T +	6.415	
			LOG P(FES) = -19972.2/T +	5.880	
-3002.5 +	1.091 T -	.099 T LOG P(FE)	-60529.3/T +	21.986 -	2.000 LOG P(FE)
-3016.0 +	1.226 T -	.099 T LOG P(FE)	-60802.1/T +	24.714 -	2.000 LOG P(FE)
-3015.2 +	1.221 T -	.099 T LOG P(FE)	-60784.2/T +	24.625 -	2.000 LOG P(FE)
-2999.9 +	1.170 T -	.099 T LOG P(FE)	-60477.3/T +	23.595 -	2.000 LOG P(FE)
-2950.9 +	1.072 T -	.099 T LOG P(FE)	-59489.0/T +	21.618 -	2.000 LOG P(FE)
-2902.8 +	1.024 T -	.099 T LOG P(FE)	-58519.5/T +	20.649 -	2.000 LOG P(FE)
-2671.1 +	.866 T -	.099 T LOG P(FE)	-53848.9/T +	17.456 -	2.000 LOG P(FE)
-2583.6 +	.822 T -	.099 T LOG P(FE)	-52084.5/T +	16.574 -	2.000 LOG P(FE)
-2750.6 +	.997 T -	.087 T LOG P(FE)	-55652.2/T +	20.102 -	1.754 LOG P(FE)
-2772.5 +	1.116 T -	.087 T LOG P(FE)	-55892.6/T +	22.506 -	1.754 LOG P(FE)
-2770.5 +	1.106 T -	.087 T LOG P(FE)	-55851.9/T +	22.303 -	1.754 LOG P(FE)
-2760.7 +	1.073 T -	.087 T LOG P(FE)	-55654.1/T +	21.640 -	1.754 LOG P(FE)
-2714.0 +	.980 T -	.087 T LOG P(FE)	-54712.6/T +	19.757 -	1.754 LOG P(FE)
-2694.8 +	.961 T -	.087 T LOG P(FE)	-54325.6/T +	19.370 -	1.754 LOG P(FE)
-556.3 +	144 T +	.099 T LOG(P(FES)/P(FE))	-11214.7/T +	2.894 +	2.000 LOG(P(FES)/P(FE))
-551.2 +	192 T +	.099 T LOG(P(FES)/P(FE))	-11313.1/T +	3.877 +	2.000 LOG(P(FES)/P(FE))
-563.6 +	205 T +	.099 T LOG(P(FES)/P(FE))	-11362.7/T +	4.126 +	2.000 LOG(P(FES)/P(FE))
-565.6 +	211 T +	.099 T LOG(P(FES)/P(FE))	-11402.2/T +	4.258 +	2.000 LOG(P(FES)/P(FE))
-553.3 +	219 T +	.099 T LOG(P(FES)/P(FE))	-11446.9/T +	4.388 +	2.000 LOG(P(FES)/P(FE))
-577.7 +	227 T +	.099 T LOG(P(FES)/P(FE))	-11446.6/T +	4.567 +	2.000 LOG(P(FES)/P(FE))
-625.9 +	251 T +	.099 T LOG(P(FES)/P(FE))	-12615.4/T +	5.052 +	2.000 LOG(P(FES)/P(FE))

N°	Equilibria	Temperature range (°K)	Equilibrium	Formulae
11	(FE) / (S ₂), Fe	0 - 100	-98740 + 31.520 T +	4.576 T LOG(P(S ₂)/P(FE))
		100 - 200	-99198 + 36.100 T +	4.576 T LOG(P(S ₂)/P(FE))
		200 - 298	-99294 + 36.582 T +	4.576 T LOG(P(S ₂)/P(FE))
		298 - 500	-99268 + 36.495 T +	4.576 T LOG(P(S ₂)/P(FE))
		500 - 1000	-98763 + 35.484 T +	4.576 T LOG(P(S ₂)/P(FE))
		1000 - 1809	-95761 + 32.483 T +	4.576 T LOG(P(S ₂)/P(FE))
		1809 - 2000	-89714 + 29.140 T +	4.576 T LOG(P(S ₂)/P(FE))
		2000 - 3500	-86139 + 27.352 T +	4.576 T LOG(P(S ₂)/P(FE))
12	(FE) / (S ₁), Fe	0 - 100	-96790 + 44.040 T +	9.151 T LOG(P(S ₁)/P(FE))
		100 - 200	-97304 + 49.180 T +	9.151 T LOG(P(S ₁)/P(FE))
		200 - 298	-97100 + 48.163 T +	9.151 T LOG(P(S ₁)/P(FE))
		298 - 500	-96588 + 46.446 T +	9.151 T LOG(P(S ₁)/P(FE))
		500 - 1000	-94842 + 42.952 T +	9.151 T LOG(P(S ₁)/P(FE))
		1000 - 1809	-87967 + 36.072 T +	9.151 T LOG(P(S ₁)/P(FE))
		1809 - 2000	-75394 + 29.127 T +	9.151 T LOG(P(S ₁)/P(FE))
		2000 - 3500	-67257 + 25.359 T +	9.151 T LOG(P(S ₁)/P(FE))
13	(FE) / (S ₂), FeS	0 - 100	-92319 + 33.540 T +	3.050 T LOG(P(S ₂)/P(FE))
		100 - 200	-92734 + 37.690 T +	3.050 T LOG(P(S ₂)/P(FE))
		200 - 298	-92708 + 37.561 T +	3.050 T LOG(P(S ₂)/P(FE))
		298 - 500	-92238 + 35.985 T +	3.050 T LOG(P(S ₂)/P(FE))
		500 - 1000	-90732 + 32.972 T +	3.050 T LOG(P(S ₂)/P(FE))
		1000 - 1463	-89252 + 31.493 T +	3.050 T LOG(P(S ₂)/P(FE))
		1463 - 2000	-82132 + 26.626 T +	3.050 T LOG(P(S ₂)/P(FE))
		2000 - 3500	-79435 + 25.277 T +	3.050 T LOG(P(S ₂)/P(FE))
14	(FE) / (S ₂), FeS _{1.450}	0 - 100	-92478 + 33.410 T +	2.915 T LOG(P(S ₂)/P(FE))
		100 - 200	-92876 + 37.390 T +	2.915 T LOG(P(S ₂)/P(FE))
		200 - 298	-92812 + 37.071 T +	2.915 T LOG(P(S ₂)/P(FE))
		298 - 500	-92479 + 35.935 T +	2.915 T LOG(P(S ₂)/P(FE))
		500 - 1000	-90917 + 32.830 T +	2.915 T LOG(P(S ₂)/P(FE))
		1000 - 1800	-90274 + 32.188 T +	2.915 T LOG(P(S ₂)/P(FE))
15	(FE) / (S ₁), FeS	0 - 100	-88134 + 40.800 T +	4.576 T LOG(P(S ₁)/P(FE))
		100 - 200	-88557 + 45.030 T +	4.576 T LOG(P(S ₁)/P(FE))
		200 - 298	-88318 + 43.837 T +	4.576 T LOG(P(S ₁)/P(FE))
		298 - 500	-87385 + 40.708 T +	4.576 T LOG(P(S ₁)/P(FE))
		500 - 1000	-84757 + 35.450 T +	4.576 T LOG(P(S ₁)/P(FE))
		1000 - 1463	-82174 + 32.868 T +	4.576 T LOG(P(S ₁)/P(FE))
		1463 - 2000	-71226 + 25.384 T +	4.576 T LOG(P(S ₁)/P(FE))
		2000 - 3500	-66948 + 23.245 T +	4.576 T LOG(P(S ₁)/P(FE))

TABLE IV Influence of temperature on the equilibrium conditions of the considered reactions.

Approximate formulae.

IV.3 Reactions 11 to 15

(see page 5)

$E_{sse} (mv) (= \frac{RT \ln p_{S_2}}{92.242})$			$\log p_{S_2} (= \frac{RT \ln p_{S_2}}{4.5756 T})$		
-1070.4 +	.342 T +	.050 T LOG(P(S2)/P(FE))	-21579.7/T +	6.899 +	1.000 LOG(P(S2)/P(FE))
-1075.4 +	.391 T +	.050 T LOG(P(S2)/P(FE))	-21679.8/T +	7.890 +	1.000 LOG(P(S2)/P(FE))
-1076.5 +	.397 T +	.050 T LOG(P(S2)/P(FE))	-21700.8/T +	7.995 +	1.000 LOG(P(S2)/P(FE))
-1076.2 +	.396 T +	.050 T LOG(P(S2)/P(FE))	-21695.1/T +	7.976 +	1.000 LOG(P(S2)/P(FE))
-1070.7 +	.385 T +	.050 T LOG(P(S2)/P(FE))	-21984.7/T +	7.755 +	1.000 LOG(P(S2)/P(FE))
-1038.1 +	.392 T +	.050 T LOG(P(S2)/P(FE))	-20928.6/T +	7.099 +	1.000 LOG(P(S2)/P(FE))
-972.9 +	.316 T +	.050 T LOG(P(S2)/P(FE))	-19607.0/T +	6.368 +	1.000 LOG(P(S2)/P(FE))
-933.8 +	.297 T +	.050 T LOG(P(S2)/P(FE))	-19823.7/T +	5.978 +	1.000 LOG(P(S2)/P(FE))
-1049.3 +	.477 T +	.099 T LOG(P(S1)/P(FE))	-21153.5/T +	9.623 +	2.000 LOG(P(S1)/P(FE))
-1054.9 +	.533 T +	.099 T LOG(P(S1)/P(FE))	-21263.8/T +	10.748 +	2.000 LOG(P(S1)/P(FE))
-1052.7 +	.522 T +	.099 T LOG(P(S1)/P(FE))	-21221.3/T +	10.526 +	2.000 LOG(P(S1)/P(FE))
-1047.1 +	.504 T +	.099 T LOG(P(S1)/P(FE))	-21109.4/T +	10.151 +	2.000 LOG(P(S1)/P(FE))
-1028.2 +	.466 T +	.099 T LOG(P(S1)/P(FE))	-20727.8/T +	9.387 +	2.000 LOG(P(S1)/P(FE))
-993.7 +	.391 T +	.099 T LOG(P(S1)/P(FE))	-19225.2/T +	7.885 +	2.000 LOG(P(S1)/P(FE))
-917.4 +	.316 T +	.099 T LOG(P(S1)/P(FE))	-16477.4/T +	6.366 +	2.000 LOG(P(S1)/P(FE))
-735.6 +	.275 T +	.099 T LOG(P(S1)/P(FE))	-14830.2/T +	5.542 +	2.000 LOG(P(S1)/P(FE))
-1000.8 +	.364 T +	.033 T LOG(P(S2)/P(FE))	-20176.4/T +	7.330 +	.667 LOG(P(S2)/P(FE))
-1005.3 +	.409 T +	.033 T LOG(P(S2)/P(FE))	-20267.1/T +	8.237 +	.667 LOG(P(S2)/P(FE))
-1005.1 +	.407 T +	.033 T LOG(P(S2)/P(FE))	-20261.4/T +	8.209 +	.667 LOG(P(S2)/P(FE))
-1000.0 +	.390 T +	.033 T LOG(P(S2)/P(FE))	-20138.7/T +	7.865 +	.667 LOG(P(S2)/P(FE))
-983.6 +	.357 T +	.033 T LOG(P(S2)/P(FE))	-19829.5/T +	7.206 +	.667 LOG(P(S2)/P(FE))
-967.5 +	.341 T +	.033 T LOG(P(S2)/P(FE))	-19506.1/T +	6.883 +	.667 LOG(P(S2)/P(FE))
-890.4 +	.299 T +	.033 T LOG(P(S2)/P(FE))	-17950.0/T +	5.819 +	.667 LOG(P(S2)/P(FE))
-861.2 +	.274 T +	.033 T LOG(P(S2)/P(FE))	-17360.6/T +	5.324 +	.667 LOG(P(S2)/P(FE))
-1002.6 +	.362 T +	.032 T LOG(P(S2)/P(FE))	-20211.1/T +	7.302 +	.637 LOG(P(S2)/P(FE))
-1006.9 +	.405 T +	.032 T LOG(P(S2)/P(FE))	-20298.1/T +	8.172 +	.637 LOG(P(S2)/P(FE))
-1006.2 +	.402 T +	.032 T LOG(P(S2)/P(FE))	-20284.1/T +	8.102 +	.637 LOG(P(S2)/P(FE))
-1002.5 +	.390 T +	.032 T LOG(P(S2)/P(FE))	-20211.3/T +	7.858 +	.637 LOG(P(S2)/P(FE))
-995.6 +	.356 T +	.032 T LOG(P(S2)/P(FE))	-19870.0/T +	7.175 +	.637 LOG(P(S2)/P(FE))
-979.7 +	.349 T +	.032 T LOG(P(S2)/P(FE))	-19729.4/T +	7.035 +	.637 LOG(P(S2)/P(FE))
-955.5 +	.442 T +	.050 T LOG(P(S1)/P(FE))	-19261.7/T +	8.917 +	1.000 LOG(P(S1)/P(FE))
-950.1 +	.488 T +	.050 T LOG(P(S1)/P(FE))	-19354.2/T +	9.841 +	1.000 LOG(P(S1)/P(FE))
-957.5 +	.475 T +	.050 T LOG(P(S1)/P(FE))	-19301.9/T +	9.581 +	1.000 LOG(P(S1)/P(FE))
-947.3 +	.441 T +	.050 T LOG(P(S1)/P(FE))	-19098.0/T +	8.897 +	1.000 LOG(P(S1)/P(FE))
-918.9 +	.384 T +	.050 T LOG(P(S1)/P(FE))	-18523.7/T +	7.748 +	1.000 LOG(P(S1)/P(FE))
-890.9 +	.356 T +	.050 T LOG(P(S1)/P(FE))	-17959.2/T +	7.183 +	1.000 LOG(P(S1)/P(FE))
-772.2 +	.275 T +	.050 T LOG(P(S1)/P(FE))	-15566.5/T +	5.548 +	1.000 LOG(P(S1)/P(FE))
-725.8 +	.252 T +	.050 T LOG(P(S1)/P(FE))	-14631.5/T +	5.080 +	1.000 LOG(P(S1)/P(FE))

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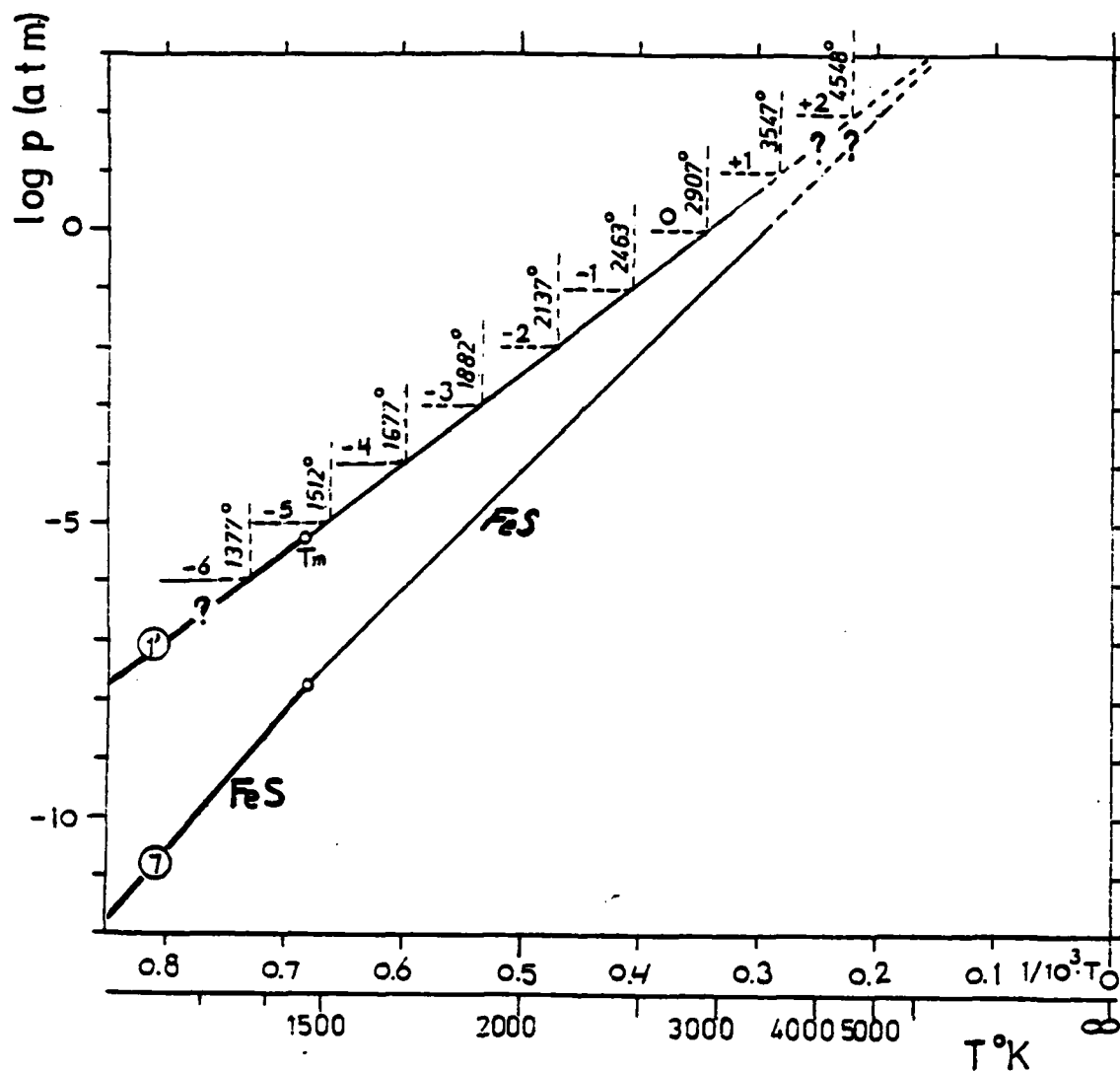


FIGURE 1 Vapor pressure and decomposition pressure of condensed FeS
(according to the data given in the JANAF tables)

line ① $\log(p_{\text{Fe}} + p_{\text{S}_2} + p_{\text{S}})$ in the presence of metallic iron
(this work p. 6)

line ⑦ $\log p_{\text{FeS}}$ (according to the JANAF tables(3), p.835,
(this work p. 6)

(see page 6)

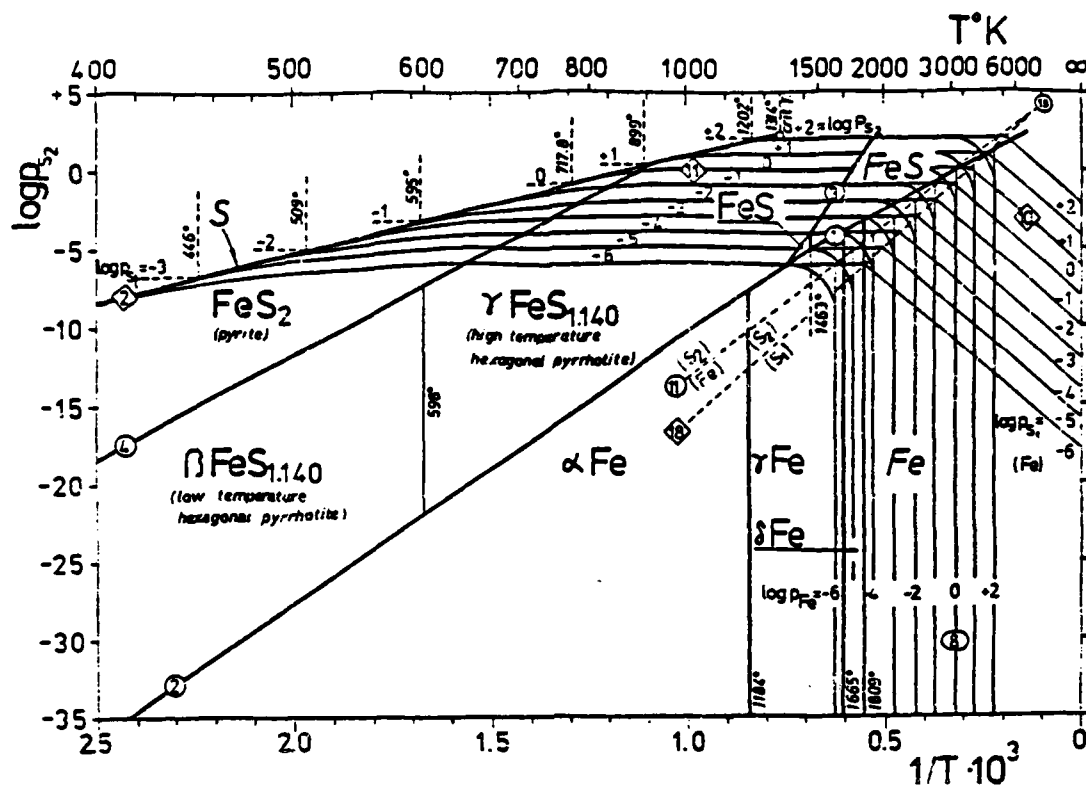


FIGURE 2 Equilibrium diagram $\log p_{S_1} = f(1/T)$ for the system S-Fe
(temperature from 400°K to infinite) (according to the
 data given in the JANAF tables) (provisional diagram)
 (see page 8)

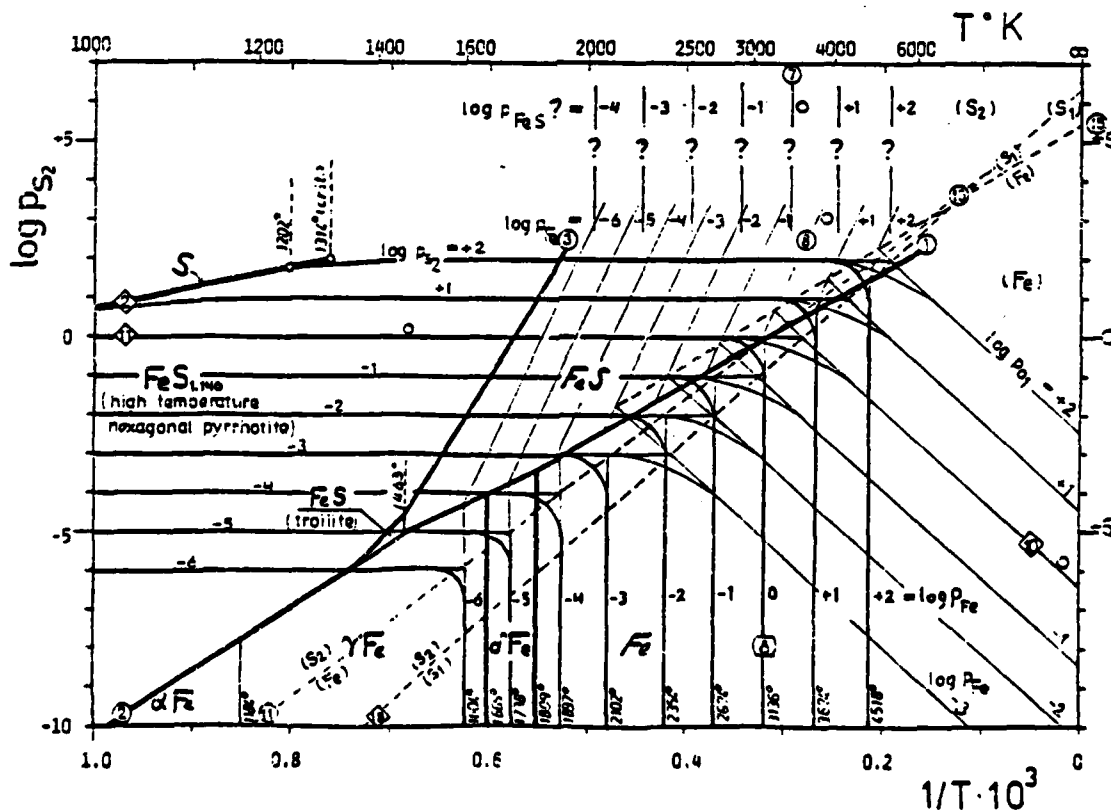
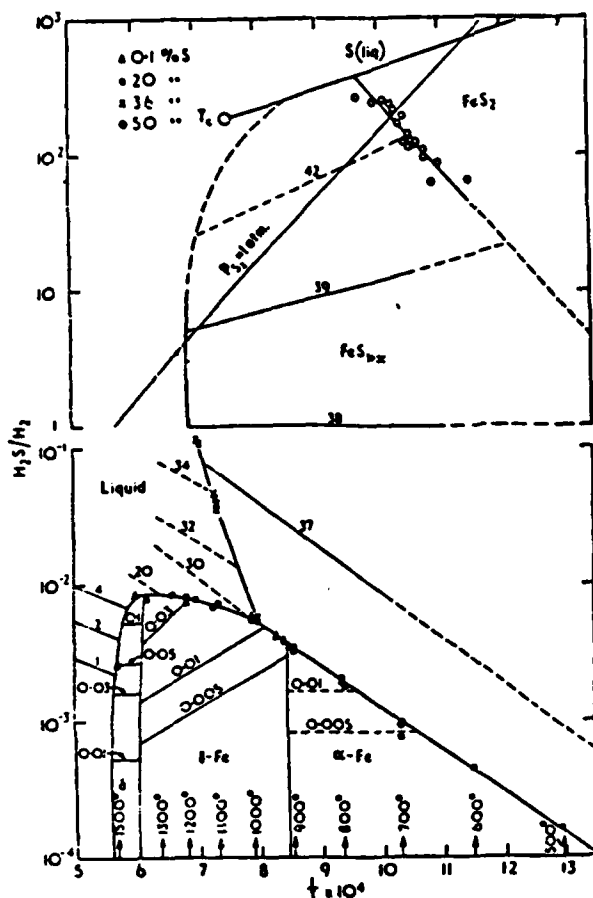
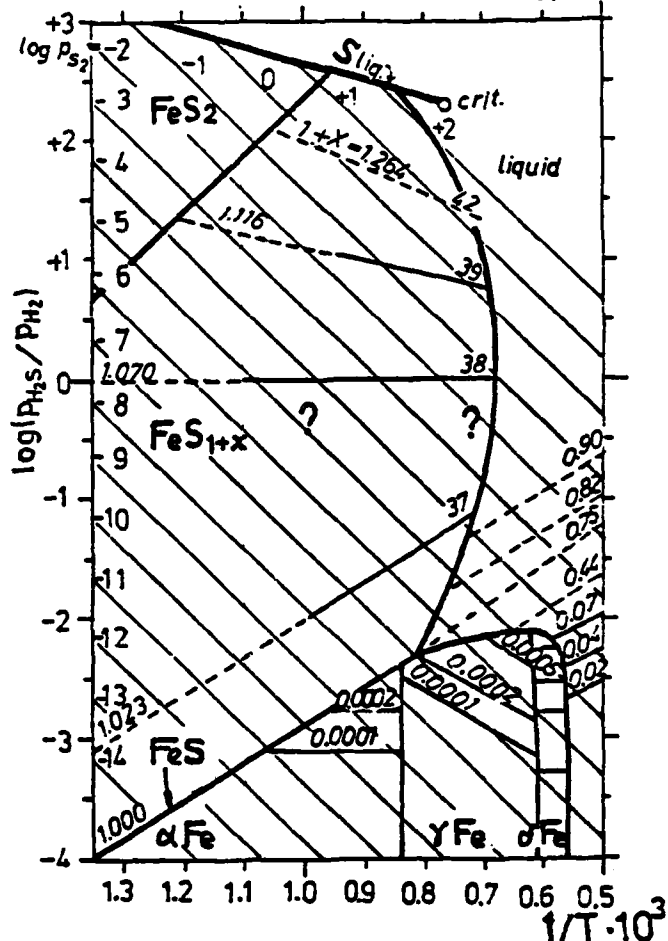


FIGURE 3 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe
(temperature from 1000°K to infinite) (according to the
data given in the JANAF tables) (provisional diagram)



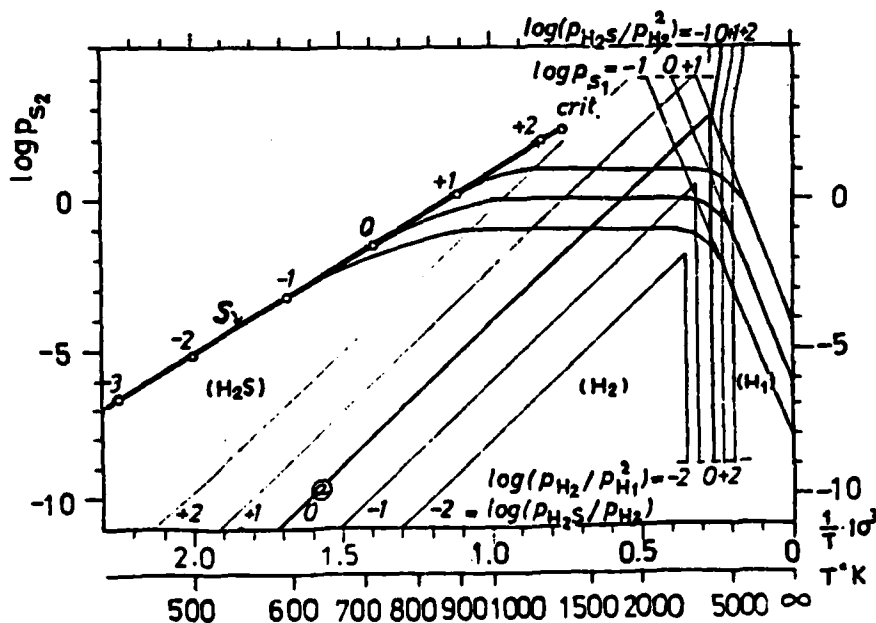
4a. Original diagram of T.ROSENQVIST(5)



4b. The same diagram with reversed scale of abscissa and with addition information

FIGURE 4 Plot of H_2S/H_2 versus $1/T$ for the system S-Fe
(composition of alloys are in wt% of sulphur)

(see page 9)

FIGURE 5 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-H
(p_{S_2} from 10^{-11} to 10^5 atm. T from 435°K to infinite)

(see page 10)

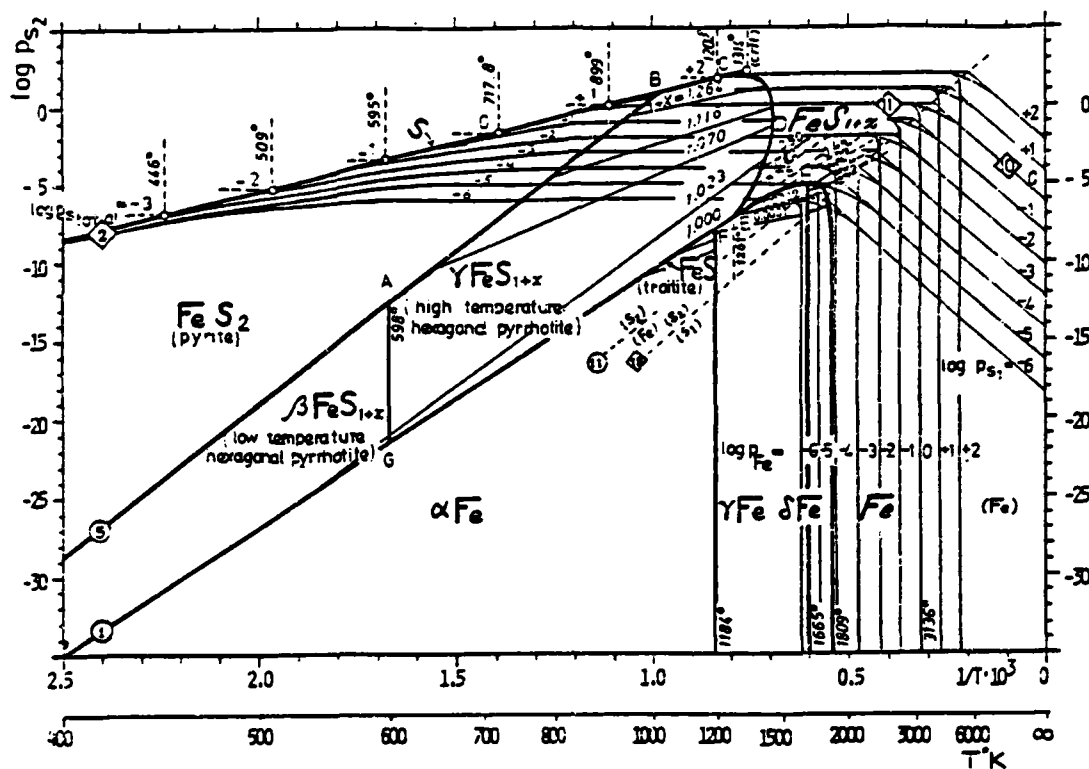


FIGURE 6 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe (revised version of figure 2)

(see page 10)

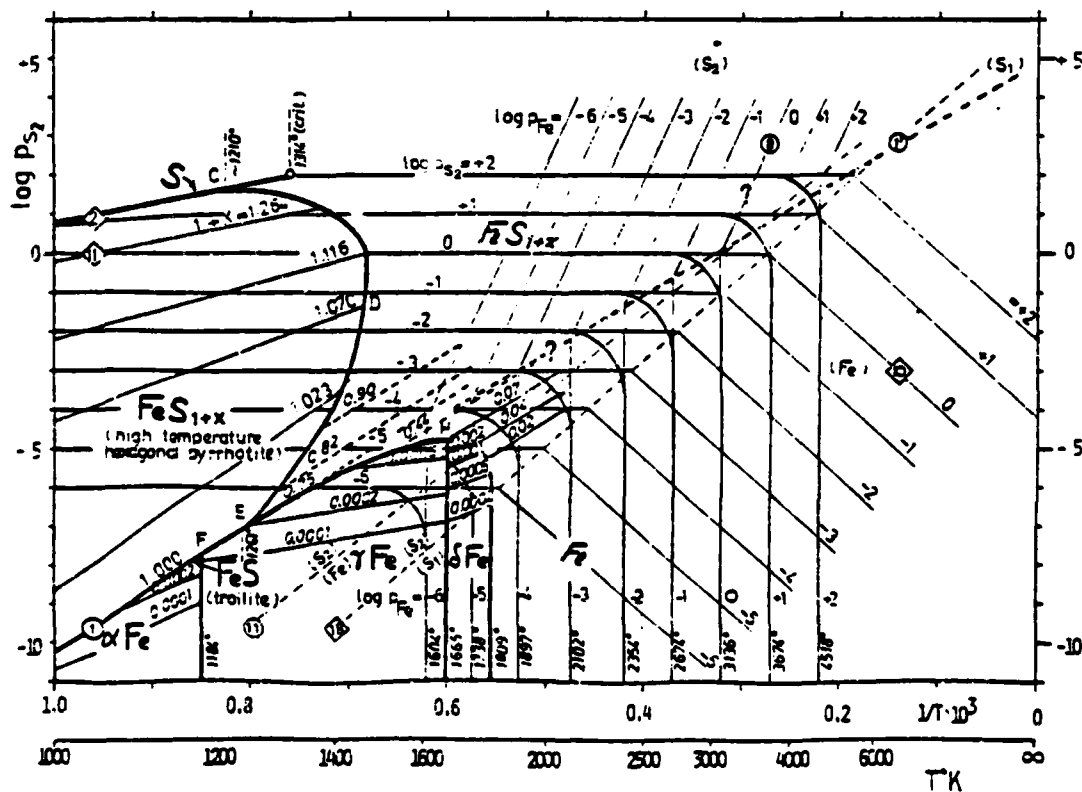


FIGURE 7 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe (revised version of figure 3)

(see page 10)

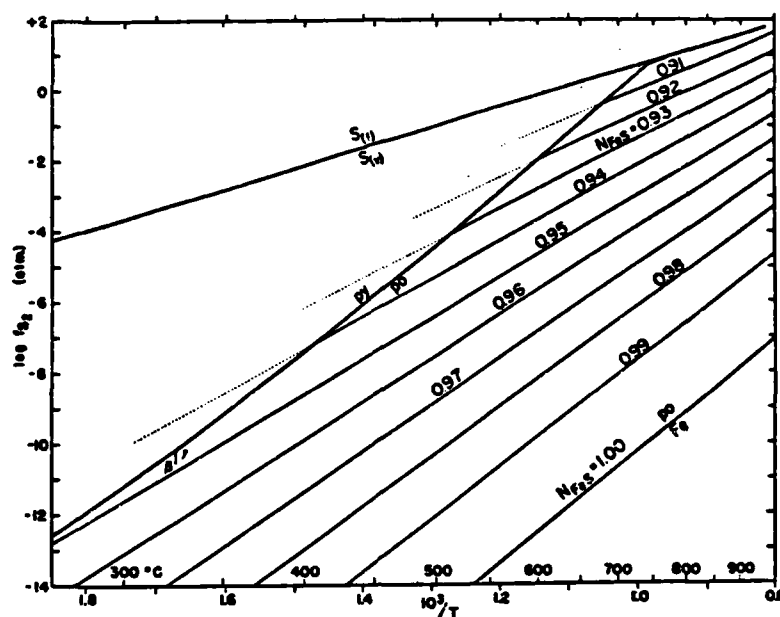


FIGURE 8 Composition of pyrrhotite in the system S-Fe
as a temperature and fugacity of (S₂)

(given by P.TOULMIN and P.B.BARTON,Jr (7))

py = pyrite

po = pyrrhotite

Fe = iron

(see page 10)

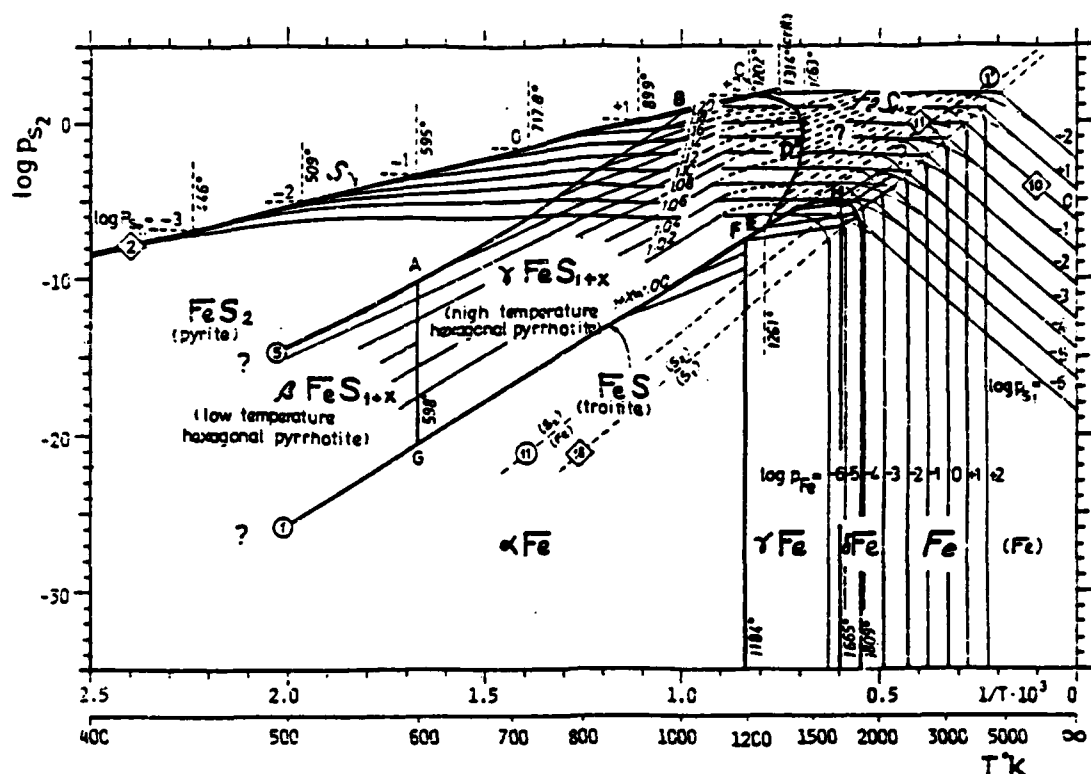


FIGURE 9 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe
(revised version of figure 6)

(see page 11)

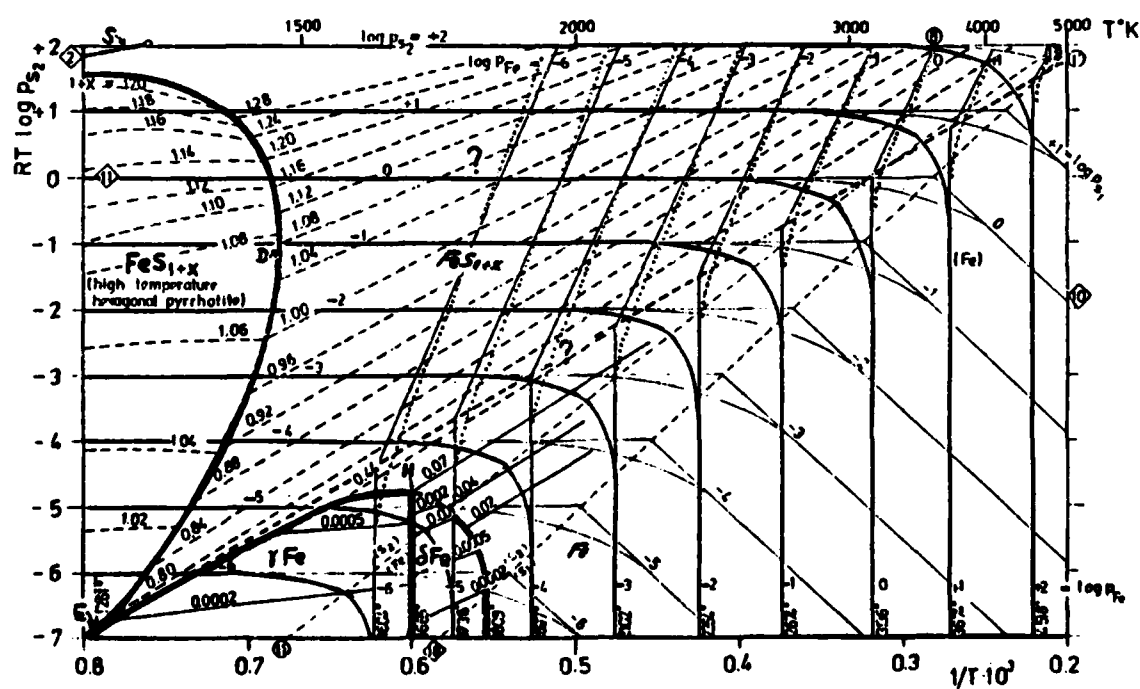


FIGURE 10 Equilibrium diagram $\log p_{S_2} = f(1/T)$ for the system S-Fe
(revised version of figure 7)

(see page 11)

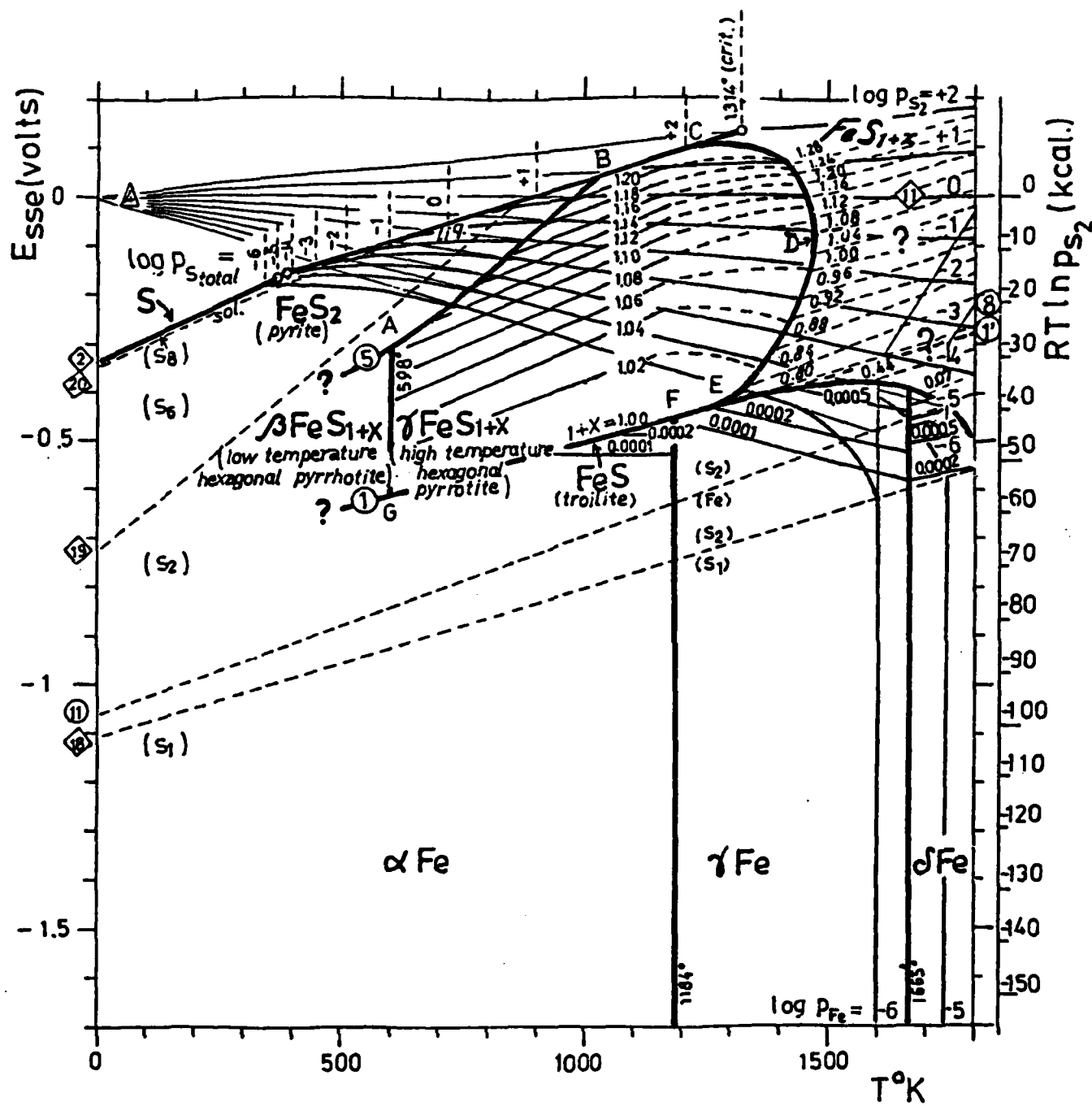
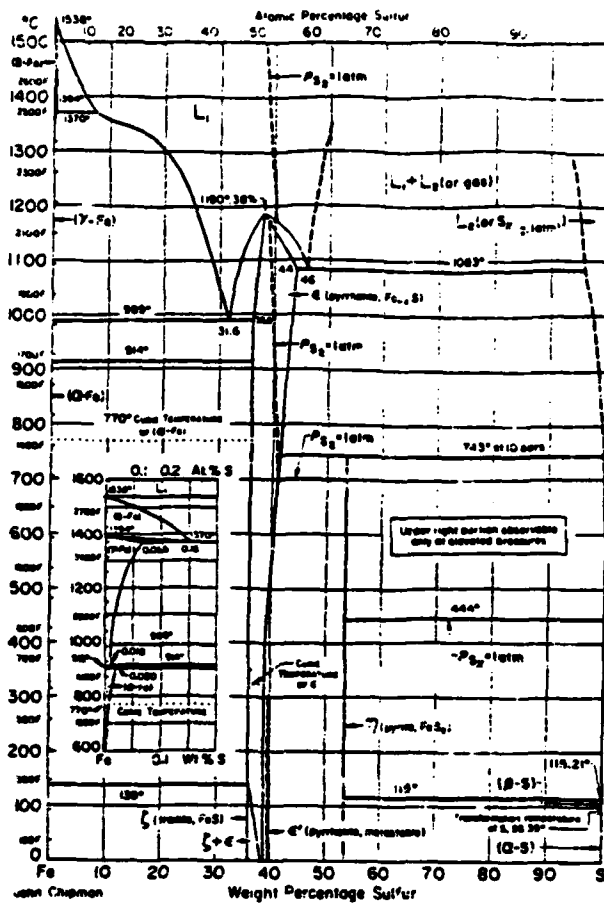


FIGURE 11 Equilibrium diagram $E_{sse} = f(T)$ for the system S-Fe

(see page 11)



12a. After John CHIPMAN

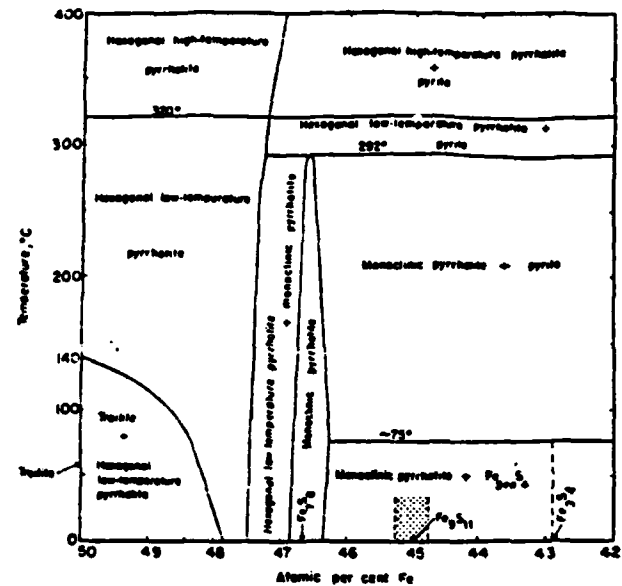
12b. A portion of the S-Fe system
at low temperatures, modified
after TAYLOR (1970)

FIGURE 12 Phase diagram of iron sulphur system

(see page 18)

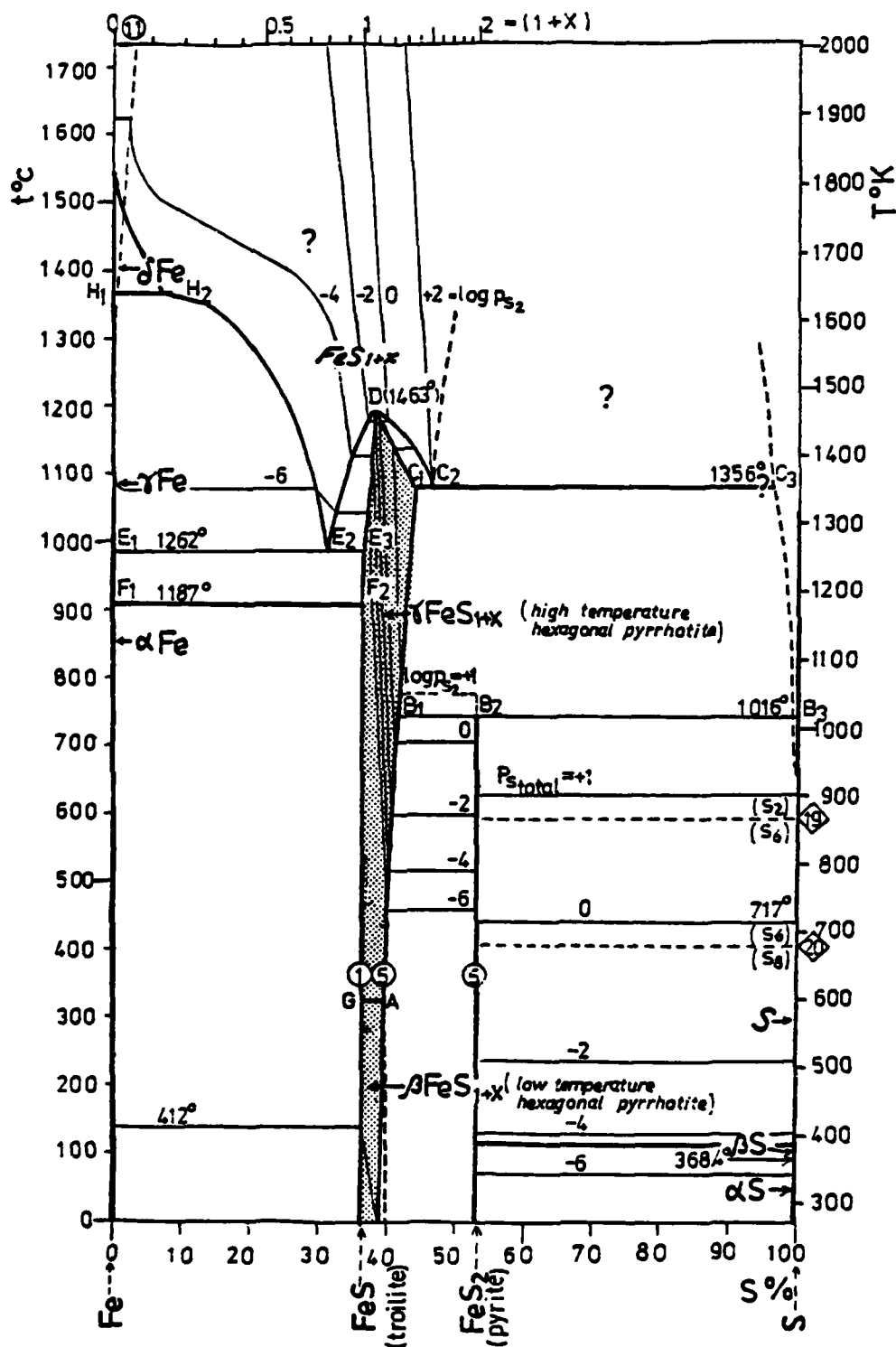


FIGURE 13 Equilibrium diagram $T = f(\text{composition})$ for the system S-Fe (revision of figure 12a)

(see page 18)

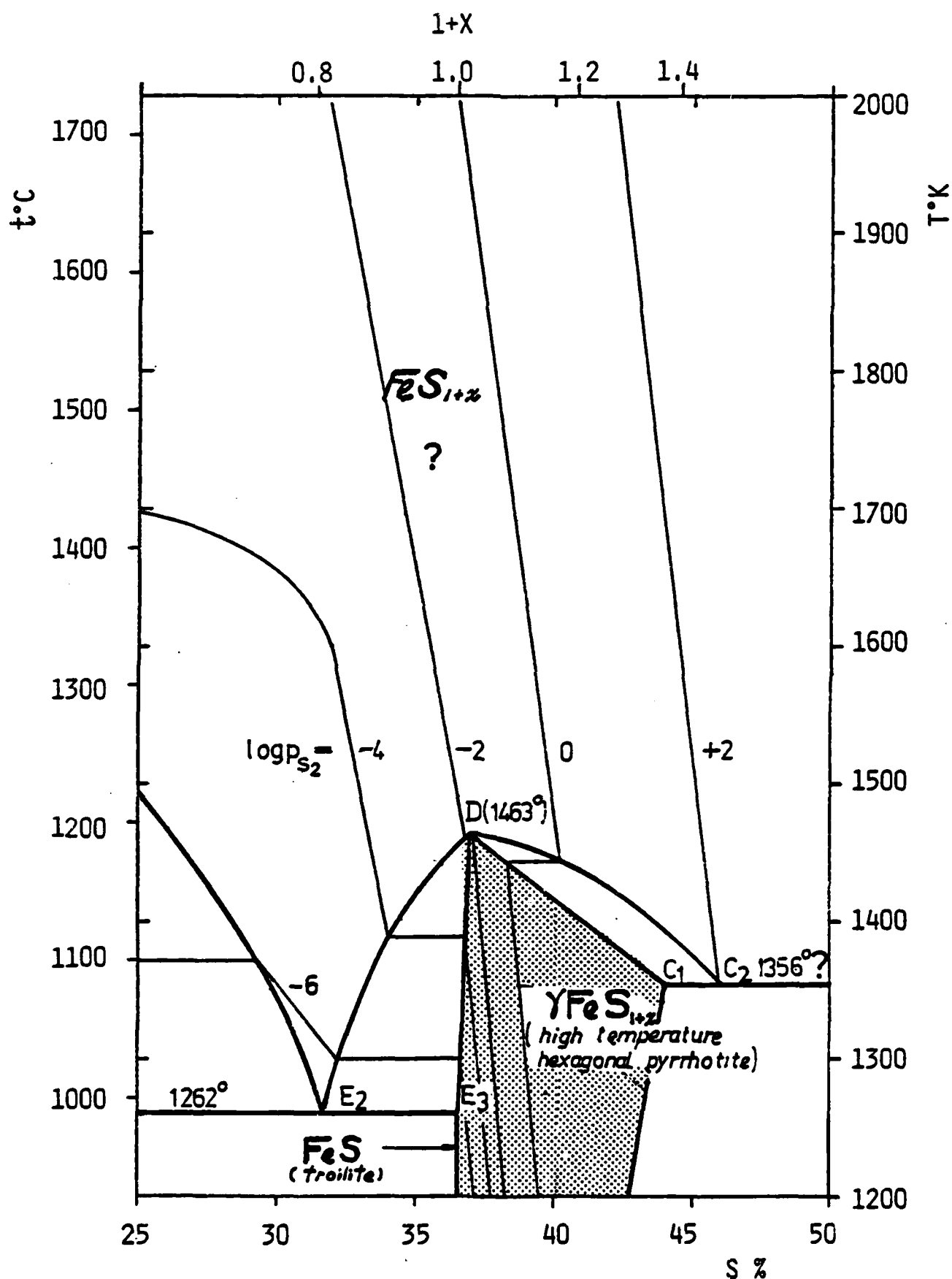


FIGURE 14 Equilibrium diagram $T = f(\text{composition})$ for the system S-Fe
(an enlargement diagram of part of figure 13)

(see page 18)

CHEMICAL AND ELECTROCHEMICAL EQUILIBRIA

IN THE PRESENCE OF A GASEOUS PHASE

O-S-Fe 13. OXYGEN-SULPHUR-IRON *

by

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SUMMARY

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* The present work is a continuation of similar work relating to systems O, H, O-Fe, O-H, O-H-Fe, C, O-C, O-C-Fe, S, O-S and S-Fe (see ref. (1) (p. 17))

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1 SUBSTANCES CONSIDERED

	<u>Considered</u>	<u>not considered</u> *
<u>Solid substances</u>		
System O	O_2, O_3	
System S	$\alpha, \beta S$	
System Fe	$\alpha, \gamma, \delta Fe$	
System O-Fe	$Fe_{1-x}O$ (wüstite) αFe_2O_3 (hematite) βFe_2O_3 (akaganeite) $\alpha, \beta Fe_3O_4$ (magnetite) $Fe_{3-\gamma}O_4$ (non-stoichiometric magnetite)	$FeO, Fe_{0.947}O$
System O-S	$SO_2, \alpha SO_3$	$\beta SO_3, \gamma SO_3$
System S-Fe	$\alpha, \beta, \gamma FeS$ (troilite) $\beta, \gamma FeS_{1.140}$ (pyrrhotite) $\beta, \gamma FeS_{1+x}$ (pyrrhotite) FeS_2 (pyrite)	$Fe_2S_3,$ FeS_2 (marcasite)
System O-S-Fe	$FeSO_4, Fe_2(SO_4)_3$	
<u>Liquid substances</u>		
System O	O_2	O_3
System S	S	
System Fe	Fe	
System O-Fe	$Fe_{1-x}O, Fe_{3-y}O_4, Fe_2O_3$	$FeO, Fe_{0.947}O$
System S-Fe	FeS, FeS_{1+x}	

* Some of these substances have been considered in previous reports (1.1 to 1.12), and omitted in the present work.

<u>considered</u>			<u>not considered</u>
<u>Gaseous substances</u>			
System	O	(O ₁), (O ₂), (O ₃)	
System	S	(S ₁), (S ₂), (S ₆), (S ₈)	(S ₃), (S ₄), (S ₅), (S ₇)
System	Fe	(Fe)	
System	O-Fe		(FeO)
System	O-S	(S ₂ O), (SO), (SO ₂), (SO ₃)	(S ₂ O ₂), (S ₂ O ₃), (S ₂ O ₇), (S ₂ O)
System	S-Fe		(FeS)

2. EQUILIBRIUM TEMPERATURES AND EQUILIBRIUM ELECTRODE
POTENTIALS OF THE CONSIDERED SUBSTANCES.
ENTHALPIES OF TRANSFORMATION.

			Equilibrium temperatures T(°K)	Equilibrium electrode potentials E	Enthalpies of transformation ΔH(cal./mole)
System	O	O ₂ / O _{2,l}	54.7	- 7.48 mv [*] _{soe}	+ 106.3
System	S	αS / βS	368.3	- 178.62 mv ^{**} _{sse}	+ 95.7
		βS / S _l	388.4	- 170.72 mv ^{**} _{sse}	+ 412.8
System	Fe	αFe / γFe	1184	—	+ 215
		γFe / δFe	1665	—	+ 200
		δFe / Fe _l	1809	—	+3300
System	O-Fe	<u>triple points</u> ***			
A.	αFe / Fe _{1-x} O / Fe ₃ O ₄		843	- 1086 mv _{soe}	—
B.	αFe / γFe / Fe _{1-x} O		1184	- 971 "	—
C.	γFe / Fe _{1-x} O / Fe _{1-x} O _l		1644	- 818 "	—
D.	γFe / δFe / Fe _{1-x} O _l		1665	- 812 "	—
E.	δFe / Fe _l / Fe _{1-x} O _l		1801	- 773 "	—
F.	Fe _{1-x} O / Fe _{1-x} O _l / Fe ₃ O ₄		1697	- 526 "	—

* This value results of formulae $\mu_{O_2}^{\circ} = -1864 + 21.464T$ (10-54.7°K)
and $\mu_{O_{2,l}}^{\circ} = -1758 + 19.520T$ (54.7-110°K)
(see ref.(1.5), p.90)

** These values result of formula $\mu_{S,l}^{\circ} = -14915 + 18.129T$ (298-500°K)
(see ref.(1.10), p. 22)

*** See ref.(1.4 , p. 47.b)

			Equilibrium temperature	Equilibrium electrode potentials	Enthalpies of transformation $\Delta H(\text{cal./mole})$
			T(°K)	E	
System	O-Fe	triple points			
G.	$\text{Fe}_{1-x}\text{O}_2 / \text{Fe}_3\text{O}_4 / \text{Fe}_{3-y}\text{O}_{4z}$	1870	- 363 mv _{soe}	—	
H.	$\text{Fe}_3\text{O}_4 / \text{Fe}_{3-y}\text{O}_4 / \text{Fe}_{3-y}\text{O}_{4z}$	1870	- 131 "	—	
J.	$\text{Fe}_{3-y}\text{O}_4 / \text{Fe}_{3-y}\text{O}_{4z} / \text{Fe}_2\text{O}_3$	1825	+ 62 "	—	
K.	$\text{Fe}_{3-y}\text{O}_{4z} / \text{Fe}_2\text{O}_3 / \text{Fe}_2\text{O}_{3z}$	1856	+ 98 "	—	
L.	$\text{Fe}_3\text{O}_4 / \text{Fe}_{3-y}\text{O}_4 / \text{Fe}_2\text{O}_3$	998	- 528 "	—	
System	O-S	$\text{SO}_2 / \text{SO}_{2,z}$	200.5	- 791.1"*	+ 1769
		$\alpha \text{SO}_3 / \text{SO}_{3,z}$	335	- 376.5"	+ 6090
System	S-Fe	triple points			
A.	$\text{FeS}_2 / \beta \text{FeS}_{1+x} / \gamma \text{FeS}_{1+x}$	598	- 310 mv _{sse} ***	—	
B.	$\text{FeS}_2 / \text{S}_2 / \gamma \text{FeS}_{1+x}$	1020?	+ 40 " ***	—	
C.	$\gamma \text{FeS}_{1+x} / \text{S}_2 / \text{FeS}_{1+xz}$	1210?	+ 100 " ***	—	
E.	$\gamma \text{FeS}_{1+x} / \gamma \text{Fe} / \text{FeS}_{1+xz}$	1261	- 430 " ***	—	
F.	$\gamma \text{FeS} / \alpha \text{Fe} / \gamma \text{Fe}$	1184	- 450 " ***	—	
G.	$\beta \text{FeS} / \gamma \text{FeS} / \alpha \text{Fe}$	598	- 610 " ***	—	
H.	$\gamma \text{Fe} / \delta \text{Fe} / \text{FeS}_{1+xz}$	1665	- 410 " ***	—	
3. THERMODYNAMIC DATA					

3. THERMODYNAMIC DATA

3.1 Standard chemical potentials μ' (or standard free enthalpies of formation $\Delta G_f'$) (tables I and II)

Tables I.1, I.2 and I.3 (pages 21 - 23) give , for different temperatures from zero till 6000°K , values of standard chemical potentials admitted for the substances considered in the present work. The values relating to substances of the one-component systems O,Fe,S and of the two-components systems O-Fe, O-S and Fe-S (columns A to I and L to Y) are those already admitted in previous reports of these series

* This value results of formula $E'_{\text{soe}, \text{SO}_{2\text{S.1}}} = -837.4 + 0.231T$ (200-298°K) (see ref.1.11, p.47)

** This value results of formula (make some slight extrapolation):

$$E'_{\text{soe}, \text{SO}_{3\text{S.1}}} = -729.6 + 1.054T \quad (200-298^\circ\text{K})$$

(see ref.1.11, p.47)

***These values are given by a graphical method according to figure 11 of system S-Fe (ref.(1.12), p. 45).

(ref. 1.1, 1.3, 1.4, 1.10, 1.11 and 1.12). The values given in columns J and K for condensed FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ are given by the JANAF tables (ref.(2)).

Tables II.1, II.2 and II.3 (pages 24 - 27) give some simplified formulae of the type $\mu' = A + BT$ (relating to given temperature ranges) for the approximate calculation of the influence of temperature on the standard chemical potentials of the considered substances.

3.2 Reactions and equilibria considered.

Formulation of the standard free enthalpies of reaction $\Delta G_r'$

Tables III.1 and III.2 (pages 28 - 31) give a list of 48 reactions and formulae which refer successively to the one component systems oxygen (where we shall consider 3 reactions with the mark Δ) and sulphur (where we shall consider 8 reactions with the mark \diamond), to the two components systems oxygen-sulphur (where we shall consider 12 reactions with the mark \square), oxygen-iron (where we shall consider 6 reactions with the mark ∇) and sulphur-iron (where we shall consider 7 reactions with the mark \nearrow), and to the three components systems oxygen-sulphur-iron (where we shall consider 12 reactions with the mark \bigcirc).

The formulae given in the third column of tables III.1 and III.2 give, for every of the considered reactions, the standard free enthalpy of reaction $\Delta G_r'$ as a function of the standard chemical potentials μ' of the considered reactants. The fourth column of these tables gives the formulae for the calculation of the free enthalpies of reaction ΔG_r as a function of their standard values ΔG_r° and of the partial pressures (or better fugacities) of the considered gaseous reactants.

For instance:

- for reaction 1 $(O_2) = O_2 \text{ s.l}$

$$\Delta G_r + RT \ln p_{O_2} = \Delta G_r^*$$

and the equilibrium condition is

$$\begin{aligned} RT \ln p_{O_2} &= \Delta G_r^* \\ \text{or } \ln p_{O_2} &= \Delta G_r^* / RT \\ \text{or } \log p_{O_2} &= \Delta G_r^* / 4.5756T \end{aligned}$$

- for reaction 18 $2(S_1) + (S_2) = 2(S_2)$

$$\Delta G_r + RT \ln p_{S_2} = \Delta G_r^* + 2 RT \ln (p_{S_2}/p_{S_1})$$

and the equilibrium condition is

$$\begin{aligned} RT \ln p_{S_2} &= \Delta G_r^* + 2 RT \ln (p_{S_2}/p_{S_1}) \\ \text{or } \ln p_{S_2} &= \Delta G_r^* / RT + 2 \ln (p_{S_2}/p_{S_1}) \\ \text{or } \log p_{S_2} &= \Delta G_r^* / 4.5756T + 2 \log (p_{S_2}/p_{S_1}) \end{aligned}$$

- for reaction 15 $2(SO) + (O_2) = 2(SO_2)$

$$\Delta G_r + RT \ln p_{O_2} = \Delta G_r^* + 2 RT \ln (p_{SO_2}/p_{SO})$$

and the equilibrium condition is

$$\begin{aligned} RT \ln p_{O_2} &= \Delta G_r^* + 2 RT \ln (p_{SO_2}/p_{SO}) \\ \text{or } \ln p_{O_2} &= \Delta G_r^* / RT + 2 \ln (p_{SO_2}/p_{SO}) \\ \text{or } \log p_{O_2} &= \Delta G_r^* / 4.5756T + 2 \log (p_{SO_2}/p_{SO}) \end{aligned}$$

- for reaction 2 $0.667 Fe_2O_3 + 2(SO_2) + (O_2) = 0.667 Fe_2(SO_4)_3$

$$\Delta G_r + RT \ln p_{O_2} = \Delta G_r^* - 2 RT \ln p_{SO_2}$$

and the equilibrium condition is

$$\begin{aligned} RT \ln p_{O_2} &= \Delta G_r^* - 2 RT \ln p_{SO_2} \\ \text{or } \ln p_{O_2} &= \Delta G_r^* / RT - 2 \ln p_{SO_2} \\ \text{or } \log p_{O_2} &= \Delta G_r^* / 4.5756T - 2 \log p_{SO_2} \end{aligned}$$

3.3 Values of the standard free enthalpies of reaction ΔG_r° , of the standard equilibrium electrode potentials E_{soe}° , and of the equilibrium gaseous pressures.

Tables IV.1 to IV.4 (pages 32 - 35) give, for the 12 reactions relating to system O-S-Fe which have been mentioned in table III.2 (page 30), the values of the standard free enthalpies of reaction ΔG_r° (calories per molar group), for given temperatures from zero to 6000°K. These data have been obtained by introducing in the formulae given in the third column of table III.2 (page 30) the values of standard chemical potentials μ° given in table I (pages 21 - 23).

These tables IV.1 to VI.4 also give, for the 11 reactions involving gaseous oxygen (O_2), i.e. for all reactions given in the lower part of table III.2 except that numbered ①, the values of the standard equilibrium electrode potentials E_{soe}° versus the standard oxygen electrode (under 1 atm. oxygen pressure at the considered temperature) and the corresponding values of the decimal logarithms of the equilibrium oxygen pressure $\log p_{O_2}$ (atm.). These values have been deduced from the values of ΔG_r° given in these tables IV.1 to IV.4 by the following formulae:

$$\begin{aligned} E_{soe}^\circ (\text{mv}) &= \frac{\Delta G_r^\circ}{92.242} \\ \log p_{O_2} (\text{atm}) &= \frac{\Delta G_r^\circ}{4.5756T} \end{aligned}$$

This table IV.1 gives, for the reaction ① which does not involve gaseous (O_2) and which involves gaseous (SO_3), the decimal logarithm of the equilibrium pressure of gaseous (SO_3). These values have been obtained by introducing in the formulae given in column 4 of table III.2 the values of ΔG_r° already given in table IV.1.

Tables V.1 and V.2 (pages 36 - 39) give, for several temperature ranges , approximate formulae for the calculation of the influence of temperature on the equilibrium conditions of 12 reactions relating to system O-S-Fe considered in table III.2 (page 30). Columns 1 ($RT \ln p_{O_2}$) and 2 (E_{soe}) relate only to reactions involving gaseous oxygen. Column 3 ($\log p$) relates to all reactions . These formulae have been obtained by introducing in the formulae given in column 4 of table III.2 (page 30), the values of ΔG_f° given in table IV (pages 32-35).

4. EQUILIBRIUM DIAGRAMS AND THEIR INTERPRETATION

Figure 1 shows, for the temperature range from zero to 1800°K and for the electrode potentials from -1.70 to +0.20 volt_{soe}, the stable equilibria of system O-Fe (ref.(1.4), Fig. 14, p.47c). Solid α, γ Fe , non-stoichiometric ferrous oxides $Fe_{1-x}O$ (wüstite), α, β Fe_3O_4 (magnetite), non-stoichiometric magnetite $Fe_{3-y}O_4$, αFe_2O_3 (hematite), βFe_2O_3 (akaganeite) , as well as gaseous (Fe) , appear on this figure 1 . We have kept for the lines drawn in this figure the numbers with which they already appeared in a previous report on system O-Fe(ref.(1.4)) and we have written these numbers inside a triangle: $\nabla 0$, $\nabla 2$

Figure 2 shows the stable equilibria of system O-S (ref.(1.11), Fig.2, p. 72) with the same coordinates as figure 1, for different gaseous pressures from 10^{-6} to 1 atm. Condensed S , SO_2 , SO_3 and gaseous species (S_8), (S_6), (S_2), (SO_2) and (SO_3) appear on this figure 2. We have kept for the lines drawn in this figure the numbers with which they already appeared in a previous report on system O-S (ref.(1.11)), and we have written these numbers inside a square $\square 1$, $\square 2$

Figure 3 is the equilibrium diagram $E = f(T)$ for the system S-Fe (temperature from zero to 1800°K, E from -1.70 to +0.20 volt_{sse}). This figure was drawn according to P.TOULMIN's and P.B.Jr.BARTON's work(ref.(5)) and to T.ROSENQVIST's work on the equilibria of system Fe/H₂S/H₂ (ref.(6)), and with the use of an equilibrium diagram for system S-H drawn in 1939 by M. POURBAIX (ref.(7)).(see ref.(1.12), p.41). It shows notably the stability of FeS₂, pyrite(between lines 2 and 5), of FeS_{1+x}, pyrrhotite (between lines 5 BCDEF and 1), of FeS, troilite(along line 1), and of Fe(below line 1, EH), as well as of gaseous (S₈), (S₆), (S₂), (S₁) and (Fe). We have kept for the lines drawn in this figure the numbers with which they already appeared in a previous report on system S-Fe (ref.(1.12)), and we have written these numbers inside a parallelogram : 1 , 5 We have not found in the literature thermodynamic data nor sufficient experimental information relating to the form of pyrrhotite stable below about 500°K ; so we have put some question-marks on this figure.

Figure 4 shows the stable equilibria relating to the three components system O-S-Fe in the presence of gaseous atmospheres containing sulphur derivatives ((SO₃), (SO₂), (S₈), (S₆) and (S₂)) under 7 different pressures (from 10⁻⁶ to 1 atm.). This figure has been obtained by superposition of figure 1 (which relates to system O-Fe) and of figure 2 (which relates to system O-S), with addition of data shown at figure 3 (which relates to system S-Fe) as well as of data concerning the stability conditions of the three components substances Fe₂(SO₄)₃ and FeSO₄.

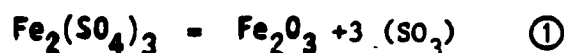
4.1 The stability and decomposition of Fe₂(SO₄)₃

At figure 4 , one sees that ferric sulphate Fe₂(SO₄)₃ is thermodynamically stable in the presence of gaseous mixtures of (SO₃), (SO₂) and (S₈) on the left-hand side of the lines of

families ①, ②, ⑤ and ⑨ corresponding to the existing pressure. This is shown more clearly at the simplified figures 6.a to 6.d, which relate respectively to a pressure of 10^{-6} , 10^{-4} , 10^{-2} and 1 atm. In this left-hand side area, Fe_2O_3 may not co-exist with gaseous (SO_3) and / or (SO_2) and may be transformed into $\text{Fe}_2(\text{SO}_4)_3$.

Figure 4 also shows that, under 1 atm. pressure, $\text{Fe}_2(\text{SO}_4)_3$ may, above -0.20 volt_{soe}, be decomposed with formation of Fe_2O_3 and (SO_3) or (SO_2) (reactions ① and ②) when heated above 900° to 1055°K (627° to 782°C). Between about -0.20 and -0.87 volt_{soe}, it may be reduced with formation of FeSO_4 and (SO_2) above about 230° to 900°K (-43° to 627°C). Below -0.87 volt_{soe}, it may theoretically be reduced with formation of FeS_2 and (S_8) , as well as of elementary S.

According to formulae given in section 1 of table V.1 (see page 37), the thermal decomposition of $\text{Fe}_2(\text{SO}_4)_3$ according to reaction



Proceeds above 640°K (367°C) with evolution of (SO_3) under the following partial pressures:

log p_{SO_3}	-6	-5	-4	-3	-2	-1	0
T($^\circ\text{K}$)	640	685	736	796	866	950	1055
$1/T \times 10^3$	1.563	1.460	1.358	1.256	1.155	1.052	0.948

These data allow to draw at figure 4 the family of vertical isobar lines ①.

In fact this reaction was used by N.LEMERY, for preparing sulphur trioxide by distillation of ferric sulphate (ref.(4), p.339).

4.2 The stability and decomposition of FeSO_4

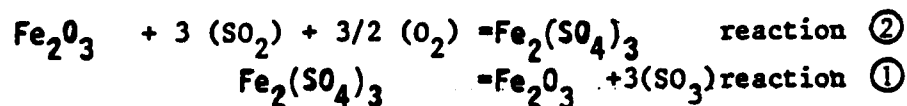
Ferrous sulphate, FeSO_4 , is the most important iron(II) sulphate. It is used for preparing other iron compounds, other sulphates, and in water treatment for avoiding the pitting corrosion of copper and copper alloys.

At figure 4 one sees that, in the presence of gaseous mixtures of (SO_3) , (SO_2) and (S_8) , ferrous sulphate is thermodynamically stable in the triangular area between lines ⑤, ③, ⑥ and ⑩. Under 1 atm., above line ⑤ of index zero, it may be oxidized into ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, and, below lines ③, ⑥, ⑩ of index zero, it may be transformed into Fe_2O_3 or FeS_2 . Ferrous sulphate decomposes with formation of Fe_2O_3 and (SO_2) from about 415°K (142°C) to 670°K (397°C) under 10^{-6} to 1 atm.

In practice, the mechanism of the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ or FeSO_4 might be more complicate than that we have just said above. Some basic sulphates, such as $\text{Fe}_2\text{O}_2(\text{SO}_4)$, are formed in these processes (ref.(3), pp.256-257 and pp.310-311). Those cases have not been considered in the present study.

4.3 Ferric oxide as a catalyst for the oxidation of (SO₂) to (SO₃)

One sees at figures 5 a and 5 b (which is an enlargement of part of figure 5 a) that, in the presence of a gas containing 5 to 15% (O₂) and 15 to 5% (SO₂)+(SO₃), under atmospheric pressure (log p = -1.3 to -0.8 for both gases), (see the shaded area), Fe₂O₃ is stable or unstable according to the temperature is higher or lower than about 905°K(632°C) to 947°K(674°C). Assuming that ferric oxide may act as a catalyst only when Fe₂O₃ and Fe₂(SO₄)₃ may be simultaneously locally stable in the gaseous atmosphere, these figures lead to the conclusion that Fe₂O₃ might be a catalyst for the oxidation of (SO₂) to (SO₃) only above the here mentioned temperature range. And this is in agreement with results shown in our previous work (see ref.(1.11), figure 10 p. 81). The catalytic action of Fe₂O₃ is then due to the following sequence of reactions:



i.e. globally: $3(\text{SO}_2) + 3/2(\text{O}_2) = 3(\text{SO}_3)$

Such a mechanism has been reported by ref.(4)(p.338).

4.4 The high temperature corrosion of iron in gaseous atmospheres containing oxygen- and sulphur derivatives

Coming back to the possible application of these diagrams to the study of corrosion phenomena, we shall take the risk of making some predictions in an area where we did not yet have the opportunity to look extensively to the literature, nor to make any experimental work: the high temperature corrosion of metals in the presence of gaseous atmospheres containing oxygen- and sulphur derivatives.

We shall assume that the corrosion behavior of

the metal very much differs according to its stable form in the existing conditions (of temperature, composition of the gaseous phase, and pressure) is the metal itself or a solid non volatile oxide (in this case corrosion is probably often not to be expected), or a salt (in this case corrosion is probably often to be expected if the temperature is high enough for allowing the formation of this salt).

In figure 6 a, which is a simplified version of the equilibrium diagram of the three components system O-S-Fe already shown in figure 4, the isobar line marked -6 relates to gaseous atmospheres where the total pressure of sulphur compounds ($(\text{SO}_3) + (\text{SO}_2) + \text{gaseous sulphur } (\text{S}_g) \text{ to } (\text{S}_2)$) is 10^{-6} atm. (i.e. for instance 2.8 mg (SO_2) per cubic meter at 0°C and 1 atm.). This isobar line separates (on its left side) a region where the stable form of iron is, according to decreasing values of the oxygen electrode potential E_{soe} , successively the salts $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , FeS_2 and $\text{FeS}_{1+\chi}$, from a region (on its right side), where its stable form is an oxide (Fe_2O_3 , Fe_3O_4 , $\text{Fe}_{1-\chi}\text{O}$) or the metal itself. These two regions are shown at figure 6 a respectively as a shaded and a not shaded area, which would, if the assumption we have just made is correct, correspond respectively to a corrosion area and to a non-corrosion area (at high temperatures). The three other diagrams drawn at figure 6 have the same significance, for pressures in total sulphur derivatives equal respectively to 10^{-4} , 10^{-2} and 1 atm.

We recall that figures 6 a to 6 d (which result of the three components equilibrium diagram for system O-S-Fe) might be valid for the behavior of iron in atmospheres containing only oxygen- and sulphur derivatives. For atmospheres containing also hydrogen derivatives, such as (H_2O) and (H_2S) , figure 6 should be replaced by other figures, which should result from the equilibrium diagram for the four components system O-H-S-Fe, which has not yet been set-up.

It is likely that, in case figures 5 and 6 would prove to be useful, the setting up of similar diagrams relating to other metals (for instance Al, Co, Cr, Mo, Ni, Si, Ti, Zr, W) would also be useful.

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Condensed substances									
	A	B	C	D	E	F	G	H	I
T°K	O ₂ (S.L)	O ₃ (S.L)	S(S.L)	SO ₂ (S.L)	SO ₃ (S.L)	Fe(S.L)	FeS(S.L)	FeS _{1.140}	FeS ₂
0	S. -1864		0	-79116	-109755	0	-24421	-28976	-40121
100	L. 194	-31314	0	-76047	-103649	0	-24371	-28968	-39848
200		-28750	0	S. -72978	-96908	0	-24356	-29019	-39120
298			0	L. -70886	-90053	0	-24368	-29123	-38256
300			α		S. -89908	0	-24368	-29125	-38239
400			L.		L. -84298	0	α -24400	-29238	-37246
500			0			0	β -24498	-29267	-35900
600			0			0	β -24630	γ -29263	-34387
700			0			0	-24780	-29278	-32769
800			-1198			0	-26103	-30631	-33466
900			258			0	-24737	-28916	-28782
1000			1678			0	-23362	-27910	-24101
1100			3067			α	0	-21950	-23422
1200			4428			γ	0	-20523	-23641
1300			5763			0	-19096	-21861	-9977
1400			7076			0	-17693	-20108	-5302
1500			8368			0	-16508	-18390	
1600						γ	0	-15662	-16710
1700						α	0	-14820	-15072
1800						δ	0	-13971	-13473
1900						L.	0	-12938	
2000						0	-11888		
2500						0	-6595		
3000						0	-1230		
3500						9593	13554		
4000									
4500									
5000									
5500									
6000									

* This formula FeS_{1.140} relates to a particular composition of the non-stoichiometric ferrous sulphide FeS_{1+x} (pyrrhotite). The corresponding values of μ' are given by the relationship $\mu'_{\text{FeS}_{1.140}} = 1.140 \times \mu'_{\text{Fe}_{0.877}\text{S}}$.

TABLE I Standard chemical potentials μ' (or standard free enthalpies of formation ΔG_f°) of the considered substances (calories·mole⁻¹).

I.1 Columns A to I

(see page 5)

	Condensed substances				Gaseous substances			
	J	K	L	M	N	O	P	Q
T °K	FeSO4	Fe2(SO4)3	Fe3O4	Fe2O3	(O1)	(O2)	(O3)	(S1)
0	-219730		-266398	-195757	58984	0	34739	63663
100	-213311		-259592	-190611	57988	0	37573	62885
200	-205305		-251358	-184182	56728	0	37411	59706
298	-197176	-540882	-243191	-177719	55390	0	38997	56533
300	-197022	-540408	-243038	-177598	55364	0	39028	56473
400	-188668	-514624	-234820	-171081	53942	0	40684	53251
500	-180178	-488343	-226772	-164681	52480	0	42351	50189
600	-171685	-461962	-218926	-158409	50991	0	44015	47205
700	-163195	-435521	-211290	-152253	49481	0	45672	44268
800	-156037	-413004	-203874	-146206	47955	0	47321	40171
900	-146185	-382362	-196661	-140248	46418	0	48963	38757
1000	-136392	-351860	-189341	-134363	44870	0	50599	37334
1100	-126629	-321449	-182336	-128461	43314	0	52227	35904
1200	-116906	-291136	-175096	-122540	41751	0	53850	34469
1300	-107235	-260947	-167849	-116616	40181	0	55468	33028
1400	-97631	-230919	-160646	-110728	38607	0	57080	31585
1500	-88091	-201038	-153483	-104872	37027	0	58688	30137
1600	-78608	-171287	-146350	-99040	35444	0	60293	28687
1700	-69176	-141657	-139227	-93222	33857	0	61895	27234
1800	-59782	-112124	-132079	-87396	32267	0	63492	25779
1900	-50247	-82326	-124380	-81208	30673	0	65088	24323
2000	-40743	-52610	-116627	-74994	29078	0	66680	22865
2500			-77685	-43922	21068	0	74623	15554
3000			-38448		13023	0	82557	8217
3500					4959	0	90496	836
4000					-3119	0	98464	-6527
4500					-11206	0	106468	-13931
5000					-19300	0	114504	-21354
5500					-27399	0	122585	-28791
6000					-35502	0	130695	-36239

TABLE I Standard chemical potentials μ' (or standard free enthalpies of formation $\Delta G'_f$) of the considered substances
I.2 Columns J to Q

(see page 5)

T° K	Gaseous substances							
	R	S	T	U	V	W	X	Y
	(S2)	(S6)	(S8)	(S20)	(S0)	(S02)	(S03)	(FE)
0	30636			-13016	1200	-70341	-93220	98740
100	26980			-15610	-786	-70966	-92203	95388
200	22923			-18240	-2953	-71425	-90555	91978
298	19027	12014	11169	-20665	-3030	-71741	-88689	88393
300	18955	11942	11094	-20709	-3069	-71746	-88652	88325
400	15131	8275	7348	-23011	-7109	-71947	-86597	84668
500	11702	5661	4972	-24899	-8943	-71923	-84310	81021
600	8479	3562	3255	-26589	-10677	-71790	-81919	77396
700	5387	1781	1941	-28099	-12321	-71562	-79441	73804
800	0	-6758	-8403	-32089	-15203	-72574	-78213	70248
900	0	665	2518	-30554	-15321	-70822	-74230	66736
1000	0	8029	13347	-29022	-15440	-69071	-70260	63279
1100	0	15347	24101	-27497	-15561	-67326	-66306	59898
1200	0	22623	34787	-25970	-15679	-65982	-62360	56578
1300	0	29856	45404	-24445	-15798	-63840	-58426	53303
1400	0	37051	55960	-22926	-15920	-62102	-54504	50052
1500	0	44213	66463	-21411	-16042	-60369	-50593	46823
1600	0	51344	76916	-19892	-16163	-58635	-46689	43617
1700	0	58443	87318	-18378	-16286	-56905	-42796	40438
1800	0	65518	97679	-16866	-16410	-55178	-38911	37293
1900	0	72563	107995	-15353	-16534	-53452	-35034	34341
2000	0	79583	118269	-13843	-16660	-51731	-31166	31435
2500	0			-6306	-17308	-43141	-11910	17284
3000	0			1224	-17990	-34575	7244	3647
3500	0			8753	-18708	-26026	26319	0
4000	0			16306	-19452	-17469	45368	0
4500	0			23871	-20226	-8908	64404	0
5000	0			31447	-21026	-345	83423	0
5500	0			39061	-21842	8237	102460	0
6000	0			46692	-22676	16823	121498	0

TABLE I Standard chemical potentials μ° (or standard free enthalpies of formation ΔG°_r) of the considered substances (calories·mole⁻¹).

I.3 Columns R to Y

(see page 5)

Condensed substances

A	$O_2(S.L.)$	0 - 100	$\mu_{O_2}^\circ$	= -1844	+ 20.580 T
B	$O_3(S.L.)$	100 - 200	$\mu_{O_3}^\circ$	= -33878	+ 25.640 T
		200 - 261		= -33877	+ 25.639 T
C	$S(S.L.)$	0 - 718	μ_S°	= 0	
		800 - 1000		= -12702	+ 14.380 T
		1000 - 1314		= -12319	+ 14.197 T
		1314 - 1900		= -9632	+ 12.000 T
D	$SO_2(S.L.)$	0 - 100	$\mu_{SO_2}^\circ$	= -79116	+ 30.690 T
		100 - 200		= -79116	+ 30.690 T
		200 - 201		= -78978	+ 30.000 T
		201 - 298		= -77220	+ 21.238 T
E	$SO_3(S.L.)$	0 - 100	$\mu_{SO_3}^\circ$	= -109735	+ 61.060 T
		100 - 200		= -110390	+ 67.410 T
		200 - 290		= -110388	+ 67.400 T
		290 - 298		= -119443	+ 98.625 T
		298 - 491		= -111657	+ 72.497 T
F	$Fe(S.L.)$	0 - 3999	μ_{Fe}°	= 0	
G	$FeS(S.L.)$	0 - 100	μ_{FeS}°	= -24421	+ .500 T
		100 - 200		= -24386	+ .150 T
		200 - 298		= -24331	+ -.122 T
		298 - 411		= -24333	+ -.115 T
		411 - 500		= -23840	+ -1.315 T
		500 - 598		= -23839	+ -1.316 T
		598 - 1000		= -26508	+ 3.147 T
		1000 - 1463		= -37111	+ 13.749 T
		1463 - 2000		= -30912	+ 9.512 T
H	$Fe_{1.140}$	0 - 100	$\mu_{Fe_{1.140}}^\circ$	= -28976	+ .080 T
		100 - 200		= -28917	+ .310 T
		200 - 298		= -28806	+ 1.061 T
		298 - 500		= -28910	+ .713 T
		500 - 598		= -29226	+ .082 T
		598 - 1000		= -31305	+ 3.396 T
I	FeS_2	0 - 100	$\mu_{FeS_2}^\circ$	= -40121	+ 2.730 T
		100 - 200		= -40376	+ 7.280 T
		200 - 298		= -40883	+ 8.816 T
		298 - 500		= -41731	+ 11.663 T
		500 - 1000		= -47699	+ 23.598 T
J	$FeSO_4$	0 - 100	$\mu_{FeSO_4}^\circ$	= -219730	+ 64.190 T
		100 - 200		= -221317	+ 80.060 T
		200 - 298		= -221894	+ 82.949 T
		298 - 500		= -222252	+ 84.149 T
		500 - 1000		= -223964	+ 87.572 T
		1000 - 2000		= -232041	+ 95.649 T
K	$Fe_2(SO_4)_3$	298 - 500	$\mu_{Fe_2(SO_4)_3}^\circ$	= -618390	+ 260.094 T
		500 - 1000		= -624826	+ 272.966 T
		1000 - 2000		= -651110	+ 299.250 T

TABLE II Simplified formulae for the approximate calculation
of the influence of temperature on the standard
chemical potentials μ° of the considered substances

II.1 Columns A to K

L	Fe_3O_4	C - 100	$\mu_{\text{Fe}_3\text{O}_4}^\circ$	= -266398	+	68.060 T
		100 - 200		= -267826	+	82.340 T
		200 - 298		= -268025	+	83.337 T
		298 - 500		= -267413	+	81.282 T
		500 - 900		= -267012	+	80.480 T
		900 - 1000		= -239931	+	50.390 T
		1000 - 1870		= -260741	+	71.200 T
		1870 - 2000		= -285396	+	84.385 T
		2000 - 3000		= -272985	+	78.179 T
M	Fe_2O_3	O - 100	$\mu_{\text{Fe}_2\text{O}_3}^\circ$	= -195757	+	51.460 T
		100 - 200		= -197040	+	64.290 T
		200 - 298		= -197371	+	63.949 T
		298 - 500		= -196953	+	64.545 T
		500 - 900		= -196681	+	64.000 T
		900 - 1000		= -181343	+	47.180 T
		1000 - 2000		= -193732	+	59.369 T
		2000 - 2500		= -199282	+	62.144 T
		<u>Gaseous substances</u>				
N	(01)	O - 100	$\mu_{(\text{o}_1)}^\circ$	= 38984	+	-9.960 T
		100 - 200		= 39248	+	-12.600 T
		200 - 298		= 39458	+	-13.653 T
		298 - 500		= 39682	+	-14.406 T
		500 - 1000		= 60090	+	-15.220 T
		1000 - 2000		= 60662	+	-15.792 T
		2000 - 5000		= 61330	+	-16.126 T
O	(02)	O - 5000	$\mu_{(\text{o}_2)}^\circ$	= 0		
P	(03)	O - 100	$\mu_{(\text{o}_3)}^\circ$	= 34739	+	28.340 T
		100 - 200		= 37735	+	-1.620 T
		200 - 298		= 34174	+	16.184 T
		298 - 500		= 34049	+	16.604 T
		500 - 1000		= 34103	+	16.496 T
		1000 - 2000		= 34518	+	16.081 T
		2000 - 5000		= 34797	+	15.941 T
Q	(S1)	O - 100	$\mu_{(\text{s}_1)}^\circ$	= 65663	+	-27.780 T
		100 - 200		= 66064	+	-31.790 T
		200 - 298		= 66181	+	-32.378 T
		298 - 500		= 65891	+	-31.406 T
		500 - 1000		= 63044	+	-25.710 T
		1000 - 2000		= 51803	+	-14.469 T
		2000 - 5000		= 52344	+	-14.740 T
R	(S2)	O - 100	$\mu_{(\text{s}_2)}^\circ$	= 30636	+	-36.360 T
		100 - 200		= 31037	+	-40.570 T
		200 - 298		= 30874	+	-39.755 T
		298 - 500		= 29833	+	-36.262 T
		500 - 718		= 28846	+	-34.289 T
		800 - 5000		= 0		

TABLE II Simplified formulae for the approximate calculation
of the influence of temperature on the standard
chemical potentials μ° of the considered substances
 II.2 Columns L to R

(see page 5)

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S	(S ₆)	298 - 300	$\mu'_{(S_6)}$	=	21384	+	-31.450 T
		500 - 1000		=	3293	+	4.736 T
		1000 - 2000		=	-63525	+	71.554 T
T	(S ₈)	298 - 300	$\mu'_{(S_8)}$	=	20311	+	-30.678 T
		500 - 1000		=	-3403	+	16.750 T
		1000 - 2000		=	-91575	+	104.922 T
U	(S ₂ O)	0 - 100	$\mu'_{(S_2O)}$	=	-13016	+	-25.940 T
		100 - 200		=	-12980	+	-26.300 T
		200 - 298		=	-13291	+	-24.745 T
		298 - 300		=	-14418	+	-20.960 T
		500 - 1000		=	-20776	+	-8.246 T
		1000 - 2000		=	-44201	+	15.179 T
		2000 - 3000		=	-44036	+	15.077 T
V	(SO)	0 - 100	$\mu'_{(SO)}$	=	1200	+	-19.840 T
		100 - 200		=	1381	+	-21.670 T
		200 - 298		=	1285	+	-21.194 T
		298 - 300		=	742	+	-19.371 T
		500 - 1000		=	-2446	+	-12.994 T
		1000 - 2000		=	-14220	+	-1.220 T
W	(SO ₂)	0 - 100	$\mu'_{(SO_2)}$	=	-70341	+	-6.250 T
		100 - 200		=	-70507	+	-4.990 T
		200 - 298		=	-70780	+	-3.224 T
		298 - 300		=	-71472	+	-901 T
		500 - 1000		=	-74775	+	5.704 T
		1000 - 2000		=	-86411	+	17.340 T
X	(SO ₃)	0 - 100	$\mu'_{(SO_3)}$	=	-93220	+	10.150 T
		100 - 200		=	-93855	+	16.500 T
		200 - 298		=	-94363	+	19.041 T
		298 - 300		=	-95149	+	21.678 T
		500 - 1000		=	-98360	+	28.100 T
		1000 - 2000		=	-109354	+	39.094 T
Y	(Fe)	0 - 100	$\mu'_{(Fe)}$	=	98740	+	-31.520 T
		100 - 200		=	99198	+	-34.100 T
		200 - 298		=	99294	+	-36.582 T
		298 - 300		=	99268	+	-36.495 T
		500 - 1000		=	98763	+	-35.484 T
		1000 - 2000		=	95123	+	-31.844 T
		2000 - 3136		=	89554	+	-29.060 T
		3500 - 3000		=	0		

TABLE II Simplified formulae for the approximate calculation
of the influence of temperature on the standard
potentials μ' of the considered substances

II.3 Columns S to Y

(see page 6)

Equilibria	Reactions
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SYSTEM OXYGEN

Reaction involving 1 condensed substance	
$\Delta_1 \text{O}_2 \text{ s.l.}$	$(\text{O}_2) = \text{O}_2 \text{ s.l.}$
Reactions involving 1 gaseous substance	
$\Delta_2 (\text{O}_2)$	$(\text{O}_2) = 2(\text{O}_1)$
$\Delta_3 (\text{O}_2)$	$(\text{O}_2) = (\text{O}_2)$

SYSTEM SULPHUR

Reactions involving 1 condensed substance	
$\Delta_4 \text{S} / (\text{S}_2)$	$2 \text{S} = (\text{S}_2)$
$\Delta_5 \text{S} / (\text{S}_6)$	$6 \text{S} = (\text{S}_6)$
$\Delta_6 \text{S} / (\text{S}_8)$	$8 \text{S} = (\text{S}_8)$
$\Delta_7 \text{S} / (\text{S}_{\text{total}})$	$n \text{S} = (\text{S}_{\text{total}})$
Reactions involving 1 or 2 gaseous substances	
$\Delta_8 (\text{S}_2)$	$(\text{S}_2) = (\text{S}_2)$
$\Delta_9 (\text{S}_1) / (\text{S}_2)$	$2(\text{S}_1) + (\text{S}_2) = 2(\text{S}_2)$
$\Delta_{10} (\text{S}_2) / (\text{S}_6)$	$\frac{1}{2}(\text{S}_2) + (\text{S}_2) = \frac{1}{2}(\text{S}_6)$
$\Delta_{11} (\text{S}_6) / (\text{S}_8)$	$(\text{S}_6) + (\text{S}_2) = (\text{S}_8)$

SYSTEM OXYGEN- SULPHUR

Reactions involving 2 condensed substances	
$\Delta_{12} \text{S} / \text{SO}_2$	$\text{S} + (\text{O}_2) = \text{SO}_2$
$\Delta_{13} \text{SO}_2 / \text{SO}_3$	$2 \text{SO}_2 + (\text{O}_2) = 2 \text{SO}_3$
Reactions involving 2 gaseous substances	
$\Delta_{14} (\text{S}_1) / (\text{SO})$	$2(\text{S}_1) + (\text{O}_2) = 2(\text{SO})$
$\Delta_{15} (\text{S}_2) / (\text{SO})$	$(\text{S}_2) + (\text{O}_2) = 2(\text{SO})$
$\Delta_{16} (\text{S}_2) / (\text{SO}_2)$	$\frac{1}{2}(\text{S}_2) + (\text{O}_2) = (\text{SO}_2)$
$\Delta_{17} (\text{SO}) / (\text{SO}_2)$	$2(\text{SO}) + (\text{O}_2) = 2(\text{SO}_2)$
$\Delta_{18} (\text{SO}_2) / (\text{SO}_3)$	$2(\text{SO}_2) + (\text{O}_2) = 2(\text{SO}_3)$
$\Delta_{19} (\text{S}_{\text{total}}) / (\text{SO}_2)$	$(\text{S}_{\text{total}}) + (\text{O}_2) = (\text{SO}_2)$
Reactions involving 1 condensed or 1 gaseous substance	
$\Delta_{20} \text{S} / (\text{SO}_2)$	$\text{S} + (\text{O}_2) = (\text{SO}_2)$
$\Delta_{21} \text{SO}_2 / (\text{SO}_2)$	$\text{SO}_2 = (\text{SO}_2)$
$\Delta_{22} \text{SO}_3 / (\text{SO}_3)$	$\text{SO}_3 = (\text{SO}_3)$
$\Delta_{23} (\text{SO}_2) / \text{SO}_3$	$2(\text{SO}_2) + (\text{O}_2) = 2 \text{SO}_3$

TABLE III Equilibria, reactions and formulae for the

III.1 Reactions relating to systems O, S and O-S

(see page 6)

ΔG° (calories per molar group)	Equilibrium formulae [*]
$\mu_{O_2}^{s.l.}$ $2 \mu_{(O_1)}^\circ$ 0	$RT \ln p_{O_2} = \Delta G_r^\circ$ $" = \Delta G_r^\circ + 9.1512 T \log p_{O_1}$ $" = 0 + 4.5756 T \log p_{O_2}$
$\mu_{(S_2)}^\circ - 2 \mu_s^\circ$ $\mu_{(S_6)}^\circ - 6 \mu_s^\circ$ $\mu_{(S_8)}^\circ - 8 \mu_s^\circ$ 0 $\mu_{(S_2)}^\circ - 2 \mu_{(S_1)}^\circ$ $1/2 \mu_{(S_2)}^\circ - 3/2 \mu_{(S_2)}^\circ$ $\mu_{(S_6)}^\circ - \mu_{(S_6)}^\circ - \mu_{(S_2)}^\circ$	$\Delta G_r^\circ = -4.5756 T \log p_{S_2}$ $\Delta G_r^\circ = -4.5756 T \log p_{S_6}$ $\Delta G_r^\circ = -4.5756 T \log p_{S_8}$ $RT \ln p_{S_2} = 0 + 4.5756 T \log p_{S_2}/p_{S_1}$ $" = \Delta G_r^\circ + 9.1512 T \log(p_{S_2}/p_{S_1})$ $" = \Delta G_r^\circ + 2.2878 T \log(p_{S_2}^2/p_{S_1})$ $" = \Delta G_r^\circ + 4.5756 T \log(p_{S_6}^6/p_{S_2}^6)$
$\mu_{SO_2}^\circ - \mu_s^\circ$ $2 \mu_{SO_3}^\circ - 2 \mu_{SO_2}^\circ$ $2 \mu_{(SO)}^\circ - 2 \mu_{(S_1)}^\circ$ $2 \mu_{(SO)}^\circ - \mu_{(S_2)}^\circ$ $\mu_{(SO_2)}^\circ - 1/2 \mu_{(S_2)}^\circ$ $2 \mu_{(SO_2)}^\circ - 2 \mu_{(SO)}^\circ$ $2 \mu_{(SO_3)}^\circ - 2 \mu_{(SO_2)}^\circ$ $\mu_{(SO_2)}^\circ - \mu_s^\circ$ $\mu_{(SO_2)}^\circ - \mu_{SO_2}^\circ$ $\mu_{(SO_3)}^\circ - \mu_{SO_3}^\circ$ $2 \mu_{SO_3}^\circ - 2 \mu_{(SO_2)}^\circ$	$RT \ln p_{O_2} = \Delta G_r^\circ$ $" = \Delta G_r^\circ$ $" = \Delta G_r^\circ + 9.1512 T \log(p_{SO}/p_{S_1})$ $" = \Delta G_r^\circ - 1.3773 T + 4.5756 T \log(\text{for } p_{SO} = p_{S_2})$ $" = \Delta G_r^\circ - 0.6887 T + 2.2878 T \log(\text{for } p_{SO_2} = p_{S_2})$ $" = \Delta G_r^\circ + 9.1512 T \log(p_{SO}/p_{SO})$ $" = \Delta G_r^\circ + 9.1512 T \log(p_{SO_2}/p_{SO_2})$ $RT \ln p_{O_2} = \Delta G_r^\circ + 4.5756 T \log p_{SO_2}$ $\Delta G_r^\circ = -4.5756 T \log p_{SO_2}$ $\Delta G_r^\circ = -4.5756 T \log p_{SO_3}$ $RT \ln p_{O_2} = \Delta G_r^\circ - 9.1512 T \log p_{SO_2}$

calculation of the equilibrium conditions

(see page 6)

* The equilibrium conditions of the considered reactions correspond to $\Delta G = 0$. For reactions where gaseous (O_2) takes part, i.e. all reactions except number ①, the values of $\Delta G + RT \ln p_{O_2}$ are thus equal to the equilibrium values of $RT \ln p_{O_2}$ (calories per mole O_2) which are shown as ordinate in the O_2 equilibrium diagrams of the type $RT \ln p_{O_2} = f(T)$. For reactions where gaseous (O_2) does not take part, the equilibrium conditions (vapor pressure, dissociation constant, etc.) are given by equaling to zero these values of $\Delta G + RT \ln p$.

Equilibria	Reactions
SYSTEM OXYGEN-IRON	
Reactions involving 2 condensed substances	
① Fe / Fe _{1-x} O	2(1-x)Fe + (O ₂) = 2 Fe _{1-x} O
② Fe / Fe ₃ O ₄	3/2 Fe + (O ₂) = 1/2 Fe ₃ O ₄
③ Fe _{1-x} O / Fe ₃ O ₄	$\frac{3}{0.5-2x}$ Fe _{1-x} O + (O ₂) = $\frac{1-x}{0.5-2x}$ Fe ₃ O ₄
④ Fe ₃ O ₄ / Fe _{3-y} O ₄	
⑤ Fe _{3-y} O ₄ / Fe ₂ O ₃	$\frac{4}{1-3y}$ Fe _{3-y} O ₄ + (O ₂) = $\frac{2(3-y)}{1-3y}$ Fe ₂ O ₃
⑥ Fe ₃ O ₄ / Fe ₂ O ₃	4 Fe ₃ O ₄ + (O ₂) = 6 Fe ₂ O ₃
SYSTEM SULPHUR-IRON	
Reactions involving 2 condensed substances	
① Fe / FeS	2 Fe + (S ₂) = 2 FeS
② Fe / FeS _{1.140}	1.754 Fe + (S ₂) = 1.754 FeS _{1.140}
③ FeS / FeS _{1.140}	14.286 FeS + (S ₂) = 14.286 FeS _{1.140}
④ FeS _{1.140} / FeS ₂	2.326 FeS _{1.140} + (S ₂) = 2.326 FeS ₂
⑤ FeS _{1+x} / FeS ₂	$\frac{2}{1-x}$ FeS _{1+x} + (S ₂) = $\frac{2}{1-x}$ FeS ₂
Reaction involving 1 condensed substance and 1 gaseous substances	
⑧ (Fe) / FeS	2 (Fe) + (S ₂) = 2 FeS
Reaction involving 1 condensed substance and 2 gaseous substances	
⑩ (Fe) / (S ₂), Fe	(Fe) + (S ₂) = Fe + (S ₂)
SYSTEM OXYGEN-SULPHUR-IRON	
Reactions involving 2 condensed substances and 1 gaseous substance	
① Fe ₂ O ₃ , (SO ₂) / Fe ₂ (SO ₄) ₃	Fe ₂ (SO ₄) ₃ = Fe ₂ O ₃ + 3 (SO ₂)
② Fe ₂ O ₃ , (SO ₂) / Fe ₂ (SO ₄) ₃	0.667 Fe ₂ O ₃ + 2(SO ₂) + (O ₂) = 0.667 Fe ₂ (SO ₄) ₃
③ Fe ₂ O ₃ , (SO ₂) / FeSO ₄	2 Fe ₂ O ₃ + 4(SO ₂) + (O ₂) = 4 FeSO ₄
④ Fe ₃ O ₄ , (SO ₂) / FeSO ₄	Fe ₃ O ₄ + 3(SO ₂) + (O ₂) = 3 FeSO ₄
⑤ FeSO ₄ , (SO ₂) / Fe ₂ (SO ₄) ₃	2 FeSO ₄ + (SO ₂) + (O ₂) = Fe ₂ (SO ₄) ₃
⑥ FeS ₂ / FeSO ₄ , (SO ₂)	0.333 FeS ₂ + (O ₂) = 0.333 FeSO ₄ + 0.333(SO ₂)
⑦ FeS ₂ / Fe ₂ O ₃ , (SO ₂)	0.365 FeS ₂ + (O ₂) = 0.183 Fe ₂ O ₃ + 0.730(SO ₂)
⑧ FeS ₂ / Fe ₃ O ₄ , (SO ₂)	0.375 FeS ₂ + (O ₂) = 0.125 Fe ₃ O ₄ + 0.750(SO ₂)
⑨ FeS ₂ / Fe ₂ (SO ₄) ₃ , (S ₈)	0.333 FeS ₂ + (O ₂) = 0.167 Fe ₂ (SO ₄) ₃ + 0.02(S ₈)
⑩ FeS ₂ / FeSO ₄ , (S ₈)	0.500 FeS ₂ + (O ₂) = 0.500 FeSO ₄ + 0.063(S ₈)
⑪ FeS _{1.140} / Fe ₃ O ₄ , (SO ₂)	0.554 FeS _{1.140} + (O ₂) = 0.185 Fe ₃ O ₄ + 0.631(SO ₂)
⑫ FeS / Fe ₃ O ₄ , (SO ₂)	0.600 FeS + (O ₂) = 0.200 Fe ₃ O ₄ + 0.600(SO ₂)

TABLE III Equilibria, reactions and formulae for the

III.2 Reactions relating to systems O-Fe,
(see page 6)

(calories ΔG° per molar group)	Equilibrium formulae
$\frac{1}{0.5-2x} ((1-x)\mu_{\text{Fe}_3\text{O}_4} - 3\mu_{\text{Fe}_{1-x}\text{O}})$ $\frac{2}{1-3y} ((3-y)\mu_{\text{Fe}_2\text{O}_3} - 2\mu_{\text{Fe}_{3-y}\text{O}_4})$ $6\mu_{\text{Fe}_2\text{O}_3} - 4\mu_{\text{Fe}_3\text{O}_4}$	$RT \ln p_{\text{O}_2} = \Delta G^\circ_r$ $" = \Delta G^\circ_r$ $" = \Delta G^\circ_r$
$2\mu_{\text{FeS}} - \mu_{\text{(S}_2)} - 2\mu_{\text{Fe}}$ $1.754\mu_{\text{FeS}_{1.140}} - \mu_{\text{(S}_2)} - 1.754\mu_{\text{Fe}}$ $14.286\mu_{\text{FeS}_{1.140}} - \mu_{\text{(S}_2)} - 14.286\mu_{\text{FeS}}$ $2.326\mu_{\text{FeS}_2} - \mu_{\text{(S}_2)} - 2.326\mu_{\text{FeS}_{1.140}}$ $2\mu_{\text{FeS}} - \mu_{\text{(S}_2)} - 2\mu_{\text{(Fe)}}$ $\mu_{\text{Fe}} - \mu_{\text{(Fe)}}$	$RT \ln p_{\text{S}_2} = \Delta G^\circ_r$ $" = \Delta G^\circ_r$ $" = \Delta G^\circ_r$ $" = \Delta G^\circ_r$ $" = \Delta G^\circ_r - 9.1512 T \log p_{\text{Fe}}$ $" = \Delta G^\circ_r + 4.5756 T \log (p_{\text{S}_2}/p_{\text{Fe}})$
$0.667\mu_{\text{Fe}_2\text{O}_3} + 3\mu_{\text{(SO}_2)} - 0.667\mu_{\text{Fe}_2(\text{SO}_4)_3}$ $4\mu_{\text{FeSO}_4} - 2\mu_{\text{(SO}_2)} - 2\mu_{\text{Fe}_2\text{O}_3}$ $3\mu_{\text{FeSO}_4} - 3\mu_{\text{(SO}_2)} - \mu_{\text{Fe}_3\text{O}_4}$ $\mu_{\text{Fe}_2(\text{SO}_4)_3} - \mu_{\text{(SO}_2)} - 2\mu_{\text{FeSO}_4}$ $0.333\mu_{\text{FeSO}_4} + 0.333\mu_{\text{(SO}_2)} - 0.333\mu_{\text{FeS}_2}$ $0.183\mu_{\text{Fe}_2\text{O}_3} + 0.730\mu_{\text{(SO}_2)} - 0.365\mu_{\text{FeS}_2}$ $0.125\mu_{\text{Fe}_3\text{O}_4} + 0.750\mu_{\text{(SO}_2)} - 0.375\mu_{\text{FeS}_2}$ $0.167\mu_{\text{Fe}_2(\text{SO}_4)_3} + 0.020\mu_{\text{(S}_8)} - 0.333\mu_{\text{FeS}_2}$ $0.500\mu_{\text{FeSO}_4} + 0.063\mu_{\text{(S}_8)} - 0.500\mu_{\text{FeS}_2}$ $0.185\mu_{\text{Fe}_3\text{O}_4} + 0.631\mu_{\text{(SO}_2)} - 0.554\mu_{\text{FeS}_{1.140}}$ $0.200\mu_{\text{Fe}_3\text{O}_4} + 0.600\mu_{\text{(SO}_2)} - 0.600\mu_{\text{FeS}}$	$\Delta G^\circ_r = -13.7268 T \log p_{\text{SO}_3}$ $RT \ln p_{\text{O}_2} = \Delta G^\circ_r - 9.1512 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r - 18.3024 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r - 13.7268 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r - 4.5756 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r + 1.5237 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r + 3.3402 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r + 3.4317 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r + 0.0916 T \log p_{\text{S}_8}$ $" = \Delta G^\circ_r + 0.2883 T \log p_{\text{S}_8}$ $" = \Delta G^\circ_r + 2.8872 T \log p_{\text{SO}_2}$ $" = \Delta G^\circ_r + 2.7454 T \log p_{\text{SO}_2}$

calculation of the equilibrium conditions

S-Fe and O-S-Fe

(see page 6)

①			②			③		
Fe2(SO4)3 / Fe2O3, (SO3)			Fe2O3, (SO2) / Fe2(SO4)3			Fe2O3, (SO2) / FeSO4		
T °K	1000/T	$\Delta Q^{\circ}(\text{CAL})$	E (MV)	LOG P _{SO3}	$\Delta Q^{\circ}(\text{CAL})$	E (MV)	LOG P _{O2}	
0	inf.							inf.
100	10.000					-2233		-411.2204
200	5.000					-2039		-182.6602
298	3.336	97096		-23.7363	-98747	-1070	-72.4202	-107.2966
300	3.333	96854		-23.5194	-98302	-1067	-71.7989	-106.2943
400	2.500	83752		-15.2334	-85249	-824	-46.5780	-68.1452
500	2.000	70732		-10.3057	-72036	-780	-31.4870	-45.3090
600	1.667	57796		-7.0174	-58889	-638	-21.4504	-30.1461
700	1.429	44945		-4.6775	-45813	-496	-14.3041	-19.3655
800	1.250	32159		-2.9285	-32806	-353	-8.7622	-11.3209
900	1.111	19424		-1.5723	-19846	-219	-4.8193	-5.0888
1000	1.000	6717		-1.4893	-6728	-75	-1.5141	-1.1220
1100	.909	-5930		.3927	5929	64	1.1780	-3.9160
1200	.833	-18484		1.1221	18710	202	3.4076	7.2457
1300	.769	-30947		1.7342	31411	340	5.2807	10.0284
1400	.714	-43321		2.2342	44036	477	6.8744	12.3856
1500	.667	-55613		2.7009	56595	613	8.2459	14.4034
1600	.625	-67820		3.0879	69081	748	9.4361	16.1438
1700	.588	-79953		3.4242	81503	883	10.4780	17.6589
1800	.556	-92005		3.7237	93862	1017	11.3964	18.9867
1900	.526	-103984		3.9870	106198	1150	12.2110	20.1568
2000	.500	-115882		4.2210	118392	1283	12.9373	21.1928

TABLE IV Standard equilibrium conditions of reaction relating to
system O-S-Fe

IV.1 Reactions 1 to 3

(see page 8)

T °K	④				⑤			⑥		
	FE3O4, (802)/FE8O4				FE8O4, (802)/FE2(804)3			FE82 / FE8O4, (802)		
	1000/T	$\Delta G^\circ(\text{CAL.})$	E (MV)	LOG PO ₂	$\Delta G^\circ(\text{CAL.})$	E (MV)	LOG PO ₂	$\Delta G^\circ(\text{CAL.})$	E (MV)	LOG PO ₂
0	inf.	-181769	-1970	inf.				-83233	-902	inf.
100	10.000	-167443	-1815	-365.9476				-81394	-882	-177.8871
200	5.000	-150282	-1629	-164.2211				-79124	-857	-86.4630
298	3.336	-133114	-1443	-97.6246	-74789	-810	-54.8496	-76810	-832	-56.3318
300	3.333	-132790	-1439	-96.7378	-74618	-808	-54.3594	-76766	-832	-55.9242
400	2.500	-115343	-1250	-63.0207	-65341	-708	-35.7008	-74381	-806	-40.6400
500	2.000	-97993	-1062	-42.8329	-56064	-607	-24.5056	-71994	-780	-31.4687
600	1.667	-80759	-875	-29.4165	-46802	-507	-17.0477	-69626	-754	-25.3613
700	1.429	-63609	-689	-19.8597	-37569	-407	-11.7296	-67262	-729	-21.0002
800	1.250	-46515	-504	-12.7073	-28356	-307	-7.7465	-64983	-704	-17.7526
900	1.111	-29428	-319	-7.1461	-19170	-207	-4.6551	-62678	-679	-15.2203
1000	1.000	-12422	-134	-2.7148	-10005	-108	-2.1866	-60393	-654	-13.1989
1100	.909	4427	47	.8796	-865	-9	-.1719	-58129	-630	-11.5492
1200	.833	21124	229	3.8472	8258	89	1.5040	-55880	-605	-10.1772
1300	.769	37664	408	6.3319	17363	188	2.9190	-53645	-581	-9.0186
1400	.714	54059	586	8.4390	26445	286	4.1283	-51425	-557	-8.0278
1500	.667	70317	762	10.2452	35513	384	5.1743			
1600	.625	86431	937	11.8060	44544	483	6.0872			
1700	.588	102414	1110	13.1663	53600	581	6.8908			
1800	.556	118267	1282	14.3596	62618	678	7.6029			
1900	.526	133995	1452	15.4130	71620	776	8.2382			
2000	.500	149591	1621	16.3466	80607	873	8.8084			

TABLE IV Standard equilibrium conditions of reaction relating to
system O-S-Fe

IV.2 Reactions 4 to 6

(see page 8)

T [°] K	1000/T	⑦				⑧				⑨		
		FeS ₂ / FeS ₂ O ₃ (802)				FeS ₂ / FeS ₂ O ₄ (802)				FeS ₂ / Fe ₂ (SO ₄) ₃ (88)		
		$\Delta G^\circ_{\text{CAL.}}$	E (mV)	LOG PO ₂		$\Delta G^\circ_{\text{CAL.}}$	E (mV)	LOG PO ₂		$\Delta G^\circ_{\text{CAL.}}$	E (mV)	LOG PO ₂
0	inf.	-72528	-786	inf.		-71010	-769	inf.				
100	10.000	-72142	-782	-157.6668		-70730	-766	-134.5808				
200	5.000	-71566	-775	-78.2040		-70318	-762	-76.8402				
298	3.336	-70930	-768	-52.0194		-69858	-757	-51.2332		-77353	-838	-56.7300
300	3.333	-70917	-768	-51.6632		-69849	-757	-50.8851		-77281	-837	-56.2994
400	2.500	-70234	-761	-38.3742		-69345	-751	-37.8885		-73384	-795	-40.0953
500	2.000	-69536	-753	-30.3943		-68826	-746	-30.0839		-69494	-753	-30.3759
600	1.667	-68844	-746	-23.0765		-68313	-740	-24.8831		-65628	-711	-23.9031
700	1.429	-68141	-738	-21.2746		-67794	-734	-21.1663		-61779	-669	-19.2883
800	1.250	-67519	-731	-18.4434		-67365	-730	-18.4033		-58003	-628	-15.8457
900	1.111	-66860	-724	-16.2359		-66905	-725	-16.2468		-54217	-587	-13.1657
1000	1.000	-66213	-717	-14.4709		-66458	-720	-14.5244		-50454	-546	-11.0268
1100	.909	-65578	-710	-13.0292		-66014	-715	-13.1158		-46718	-506	-9.2820
1200	.833	-64941	-704	-11.8274		-65568	-710	-11.9416		-43000	-466	-7.8314
1300	.769	-64302	-697	-10.8102		-65119	-705	-10.9475		-39302	-426	-6.6073
1400	.714	-63662	-690	-9.9381		-64669	-701	-10.0953		-35622	-386	-5.5609
1500	.667											
1600	.625											
1700	.588											
1800	.556											
1900	.526											
2000	.500											

TABLE IV Standard equilibrium conditions of reaction relating to
system O-S-Fe

IV.3 Reactions 7 to 9

(see page 8)

T°K	1000/T	(10)				(11)				(12)			
		FeS ₂ / FeS ₂ O ₄ (88)				FeS ₂ 140 / FeS ₂ O ₄ (802)				FeS / FeS ₂ O ₄ (802)			
		$\Delta q(\text{CAL.})$	E(MV)	LOG PO ₂		$\Delta q(\text{CAL.})$	E(MV)	LOG PO ₂		$\Delta q(\text{CAL.})$	E(MV)	LOG PO ₂	
0	<i>inf.</i>							<i>inf.</i>				<i>inf.</i>	
100	10.000					-77630	-841	-167.7813		-80831	-876	-174.5673	
200	5.000					-76770	-832	-82.5116		-79875	-865	-85.7942	
298	3.356	-78796	-853	-57.7590		-75508	-818	-94.3729		-78512	-851	-56.5159	
300	3.333	-78692	-853	-57.3273		-74139	-803	-53.9907		-77061	-835	-56.1194	
400	2.500	-75248	-815	-41.1137		-74112	-803	-39.6915		-77034	-835	-41.2470	
500	2.000	-71825	-778	-31.3945		-72645	-787	-31.0936		-75492	-818	-32.2620	
600	1.667	-68443	-741	-24.9304		-71136	-771			-73809	-800		
700	1.429	-65090	-705	-20.3221									
800	1.250	-61814	-670	-16.8869		-67603	-754	-25.3930		-72081	-781	-26.2556	
900	1.111	-58542	-634	-14.2160		-68038	-737	-21.2425		-70327	-762	-21.9572	
1000	1.000	-55304	-599	-12.0867		-66556	-721	-18.1823		-68657	-744	-18.7563	
1100	.909	-52100	-564	-10.3513		-65065	-705	-15.8000		-66983	-726	-16.2657	
1200	.833	-48921	-530	-8.9098		-63200	-685	-13.8124		-65333	-708	-14.2786	
1300	.769	-45768	-496	-7.6943									
1400	.714	-42639	-462	-6.6563		-62143	-673	-12.3467		-63692	-690	-12.6945	
1500	.667					-60689	-657	-11.0530		-62054	-672	-11.3016	
1600	.625					-59234	-642	-9.9582		-60416	-654	-10.1569	
1700	.588					-57775	-626	-9.0191		-58774	-637	-9.1751	
1800	.556					-56308	-610	-8.2041		-57013	-618	-8.3068	
1900	.526												
2000	.500					-54824	-594	-7.4886		-55053	-596	-7.5199	
2500	.400					-53321	-578	-6.8549		-53096	-575	-6.8260	
3000	.333					-51794	-561	-6.2887		-51139	-554	-6.2091	
										-49184	-533	-5.6575	
										-47231	-512	-5.1612	
										-37464	-406	-3.2751	
										-27696	-300	-2.0177	

TABLE IV Standard equilibrium conditions of reaction relating to
system O-S-Fe

N°	Equilibria	Temperature range (°K)	RT ln p _{O₂} (calories)
①	Fe ₂ (SO ₄) ₃ / Fe ₂ O ₃ , (SO ₂)	298 - 500 500 - 900 900 - 1000 1000 - 2000	
②	Fe ₂ O ₃ , (SO ₂) / Fe ₂ (SO ₄) ₃	298 - 500 500 - 900 900 - 1000 1000 - 2000	-138152 + 132.233 T - 9.151 T LOG P(SO ₂) -137273 + 130.475 T - 9.151 T LOG P(SO ₂) -136108 + 129.180 T - 9.151 T LOG P(SO ₂) -132248 + 125.320 T - 9.151 T LOG P(SO ₂)
③	Fe ₂ O ₃ , (SO ₂) / FeSO ₄	0 - 100 100 - 200 200 - 298 298 - 500 500 - 900 900 - 1000 1000 - 2000	-206042 + 178.840 T - 18.302 T LOG P(SO ₂) -209160 + 210.020 T - 18.302 T LOG P(SO ₂) -209715 + 212.796 T - 18.302 T LOG P(SO ₂) -209212 + 211.109 T - 18.302 T LOG P(SO ₂) -207035 + 206.755 T - 18.302 T LOG P(SO ₂) -204538 + 203.980 T - 18.302 T LOG P(SO ₂) -195056 + 194.498 T - 18.302 T LOG P(SO ₂)
④	Fe ₃ O ₄ , (SO ₂) / FeSO ₄	0 - 100 100 - 200 200 - 298 298 - 500 500 - 900 900 - 1000 1000 - 2000	-181769 + 143.260 T - 13.727 T LOG P(SO ₂) -184604 + 171.610 T - 13.727 T LOG P(SO ₂) -185318 + 175.184 T - 13.727 T LOG P(SO ₂) -184926 + 173.866 T - 13.727 T LOG P(SO ₂) -183699 + 171.413 T - 13.727 T LOG P(SO ₂) -182482 + 170.060 T - 13.727 T LOG P(SO ₂) -174435 + 162.013 T - 13.727 T LOG P(SO ₂)
⑤	FeSO ₄ , (SO ₂) / Fe ₂ (SO ₄) ₃	298 - 500 500 - 1000 1000 - 2000	-102413 + 92.698 T - 4.576 T LOG P(SO ₂) -102123 + 92.118 T - 4.576 T LOG P(SO ₂) -100617 + 90.612 T - 4.576 T LOG P(SO ₂)
⑥	FeS ₂ / FeSO ₄ , (SO ₂)	0 - 100 100 - 200 200 - 298 298 - 500 500 - 1000 1000 - 1400	-83233 + 18.390 T + 1.524 T LOG P(SO ₂) -83664 + 22.700 T + 1.524 T LOG P(SO ₂) -83846 + 23.612 T + 1.524 T LOG P(SO ₂) -83914 + 23.842 T + 1.524 T LOG P(SO ₂) -83595 + 23.202 T + 1.524 T LOG P(SO ₂) -82813 + 22.420 T + 1.524 T LOG P(SO ₂)
⑦	FeS ₂ / Fe ₂ O ₃ , (SO ₂)	0 - 100 100 - 200 200 - 298 298 - 500 500 - 900 900 - 1000 1000 - 1400	-72528 + 3.860 T + 3.340 T LOG P(SO ₂) -72718 + 5.760 T + 3.340 T LOG P(SO ₂) -72863 + 6.490 T + 3.340 T LOG P(SO ₂) -72986 + 6.901 T + 3.340 T LOG P(SO ₂) -72881 + 6.690 T + 3.340 T LOG P(SO ₂) -72683 + 6.470 T + 3.340 T LOG P(SO ₂) -72590 + 6.378 T + 3.340 T LOG P(SO ₂)

TABLE V Influence of temperature on the equilibrium

V.1 Reactions 1 to 7

(see page 9)

$$E_{\text{soe}}(\text{mv}) = \left(\frac{RT \ln p_{\text{O}_2}}{92.242} \right)$$

$$\log p_{\text{O}_2}(\text{atm}) = \left(\frac{RT \ln p_{\text{O}_2}}{4.5756 T} \right) \text{ (or } \log p_{\text{O}_2} \text{)}$$

-1497.7 + 1.434 T - .099 T LOG P(SO2)	LOG P(SO3) = -9906.8/T + 9.508
-1488.2 + 1.414 T - .099 T LOG P(SO2)	LOG P(SO3) = -9825.1/T + 9.344
-1475.6 + 1.400 T - .099 T LOG P(SO2)	LOG P(SO3) = -9746.4/T + 9.257
-1433.7 + 1.359 T - .099 T LOG P(SO2)	LOG P(SO3) = -9420.7/T + 8.931
-2233.7 + 1.939 T - .198 T LOG P(SO2)	
-2267.5 + 2.277 T - .198 T LOG P(SO2)	-30193.2/T + 28.900 - 2.000 LOG P(SO2)
-2273.5 + 2.307 T - .198 T LOG P(SO2)	-30001.1/T + 28.515 - 2.000 LOG P(SO2)
-2268.1 + 2.289 T - .198 T LOG P(SO2)	-29746.5/T + 28.232 - 2.000 LOG P(SO2)
-2244.5 + 2.241 T - .198 T LOG P(SO2)	-28902.9/T + 27.389 - 2.000 LOG P(SO2)
-2217.4 + 2.211 T - .198 T LOG P(SO2)	
-2114.6 + 2.109 T - .198 T LOG P(SO2)	-45030.6/T + 39.086 - 4.000 LOG P(SO2)
	-45712.0/T + 45.900 - 4.000 LOG P(SO2)
-1970.6 + 1.553 T - .149 T LOG P(SO2)	-45833.3/T + 46.507 - 4.000 LOG P(SO2)
-2001.3 + 1.860 T - .149 T LOG P(SO2)	-45723.4/T + 46.138 - 4.000 LOG P(SO2)
-2009.0 + 1.899 T - .149 T LOG P(SO2)	-45247.6/T + 45.186 - 4.000 LOG P(SO2)
-2004.8 + 1.885 T - .149 T LOG P(SO2)	-44701.9/T + 44.580 - 4.000 LOG P(SO2)
-1991.5 + 1.858 T - .149 T LOG P(SO2)	-42629.6/T + 42.508 - 4.000 LOG P(SO2)
-1978.3 + 1.844 T - .149 T LOG P(SO2)	
-1891.1 + 1.756 T - .149 T LOG P(SO2)	-39725.7/T + 31.310 - 3.000 LOG P(SO2)
	-40345.3/T + 37.505 - 3.000 LOG P(SO2)
-1110.3 + 1.005 T - .050 T LOG P(SO2)	-40501.4/T + 38.286 - 3.000 LOG P(SO2)
-1107.1 + .999 T - .050 T LOG P(SO2)	-40415.7/T + 37.999 - 3.000 LOG P(SO2)
-1090.8 + .982 T - .050 T LOG P(SO2)	-40147.5/T + 37.462 - 3.000 LOG P(SO2)
	-39881.5/T + 37.167 - 3.000 LOG P(SO2)
-902.3 + .199 T + .017 T LOG P(SO2)	-38122.9/T + 35.408 - 3.000 LOG P(SO2)
-907.0 + .246 T + .017 T LOG P(SO2)	
-909.0 + .256 T + .017 T LOG P(SO2)	-22382.4/T + 20.259 - 1.000 LOG P(SO2)
-909.7 + .258 T + .017 T LOG P(SO2)	-22319.0/T + 20.132 - 1.000 LOG P(SO2)
-906.3 + .252 T + .017 T LOG P(SO2)	-21989.9/T + 19.803 - 1.000 LOG P(SO2)
-897.8 + .243 T + .017 T LOG P(SO2)	
	-18190.6/T + 4.019 + .333 LOG P(SO2)
-786.3 + .042 T + .036 T LOG P(SO2)	-18284.8/T + 4.961 + .333 LOG P(SO2)
-788.3 + .062 T + .036 T LOG P(SO2)	-18324.6/T + 5.160 + .333 LOG P(SO2)
-789.9 + .070 T + .036 T LOG P(SO2)	-18339.5/T + 5.211 + .333 LOG P(SO2)
-791.2 + .075 T + .036 T LOG P(SO2)	-18269.7/T + 5.071 + .333 LOG P(SO2)
-790.1 + .073 T + .036 T LOG P(SO2)	-18098.8/T + 4.900 + .333 LOG P(SO2)
-788.0 + .070 T + .036 T LOG P(SO2)	
-787.0 + .069 T + .036 T LOG P(SO2)	-15851.0/T + .844 + .730 LOG P(SO2)
	-15892.6/T + 1.259 + .730 LOG P(SO2)
	-15924.3/T + 1.418 + .730 LOG P(SO2)
	-15951.1/T + 1.508 + .730 LOG P(SO2)
	-15928.2/T + 1.462 + .730 LOG P(SO2)
	-15884.9/T + 1.414 + .730 LOG P(SO2)
	-15864.6/T + 1.394 + .730 LOG P(SO2)

conditions of the considered reactions

N	Equilibria	Temperature range (°K)	RT ln p ₀₂ (calories)		
⑧	FeS ₂ / Fe ₃ O ₄ , (SO ₂)	0 - 100	-71010 +	2.800 T +	3.432 T LOG P(SO ₂)
		100 - 200	-71142 +	4.120 T +	3.432 T LOG P(SO ₂)
		200 - 298	-71256 +	4.694 T +	3.432 T LOG P(SO ₂)
		298 - 500	-71380 +	5.109 T +	3.432 T LOG P(SO ₂)
		500 - 900	-71227 +	4.803 T +	3.432 T LOG P(SO ₂)
		900 - 1000	-70928 +	4.470 T +	3.432 T LOG P(SO ₂)
		1000 - 1400	-70930 +	4.473 T +	3.432 T LOG P(SO ₂)
⑨	FeS ₂ / Fe ₂ (SO ₄) ₃ , (S ₈)	298 - 500	-88946 +	38.906 T +	.096 T LOG P(S ₈)
		500 - 1000	-88534 +	38.080 T +	.096 T LOG P(S ₈)
		1000 - 1400	-87534 +	37.080 T +	.096 T LOG P(S ₈)
⑩	FeS ₂ / Fe ₃ O ₄ , (S ₈)	298 - 500	-88980 +	34.312 T +	.288 T LOG P(S ₈)
		500 - 1000	-88346 +	33.042 T +	.288 T LOG P(S ₈)
		1000 - 1400	-86966 +	31.663 T +	.288 T LOG P(S ₈)
⑪	FeS _{1.140} / Fe ₃ O ₄ , (SO ₂)	0 - 100	-77630 +	8.600 T +	2.887 T LOG P(SO ₂)
		100 - 200	-78032 +	12.620 T +	2.887 T LOG P(SO ₂)
		200 - 298	-78301 +	13.969 T +	2.887 T LOG P(SO ₂)
		298 - 500	-78569 +	14.866 T +	2.887 T LOG P(SO ₂)
		500 - 1000	-79072 +	15.872 T +	2.887 T LOG P(SO ₂)
		1000 - 1800	-77457 +	14.258 T +	2.887 T LOG P(SO ₂)
⑫	FeS / Fe ₃ O ₄ , (SO ₂)	0 - 100	-80831 +	9.560 T +	2.745 T LOG P(SO ₂)
		100 - 200	-81238 +	13.630 T +	2.745 T LOG P(SO ₂)
		200 - 298	-81473 +	14.806 T +	2.745 T LOG P(SO ₂)
		298 - 411	-81644 +	15.382 T +	2.745 T LOG P(SO ₂)
		411 - 500	-82313 +	17.009 T +	2.745 T LOG P(SO ₂)
		500 - 1000	-82285 +	16.952 T +	2.745 T LOG P(SO ₂)
		1000 - 1463	-81730 +	16.398 T +	2.745 T LOG P(SO ₂)
		1463 - 2000	-86374 +	19.572 T +	2.745 T LOG P(SO ₂)
		2000 - 3000	-86301 +	19.535 T +	2.745 T LOG P(SO ₂)

TABLE V Influence of temperature on the

V.2 Reactions 8 to 12

(see page 9)

$E_{\text{soe}} (\text{mv}) (= \frac{RT \ln p_{\text{O}_2}}{92.242})$	$\log p_{\text{O}_2} (\text{atm}) (= \frac{RT \ln p_{\text{O}_2}}{4.5756 T})$
---	---

-769.8 + .030 T + .037 T LOG P(SO2)	-15519.3/T + .612 + .750 LOG P(SO2)
-771.3 + .045 T + .037 T LOG P(SO2)	-15548.1/T + .900 + .750 LOG P(SO2)
-772.5 + .051 T + .037 T LOG P(SO2)	-15573.0/T + 1.026 + .750 LOG P(SO2)
-773.8 + .055 T + .037 T LOG P(SO2)	-15600.1/T + 1.117 + .750 LOG P(SO2)
-772.2 + .052 T + .037 T LOG P(SO2)	-15566.7/T + 1.050 + .750 LOG P(SO2)
-768.9 + .048 T + .037 T LOG P(SO2)	-15501.4/T + .977 + .750 LOG P(SO2)
-769.0 + .048 T + .037 T LOG P(SO2)	-15501.8/T + .977 + .750 LOG P(SO2)
-964.3 + .422 T + .001 T LOG P(S8)	-19439.2/T + 8.503 + .021 LOG P(S8)
-959.8 + .413 T + .001 T LOG P(S8)	-19349.2/T + 8.322 + .021 LOG P(S8)
-949.0 + .402 T + .001 T LOG P(S8)	-19130.6/T + 8.104 + .021 LOG P(S8)
-964.6 + .372 T + .003 T LOG P(S8)	-19446.6/T + 7.499 + .063 LOG P(S8)
-957.8 + .358 T + .003 T LOG P(S8)	-19308.1/T + 7.221 + .063 LOG P(S8)
-942.8 + .343 T + .003 T LOG P(S8)	-19006.5/T + 6.920 + .063 LOG P(S8)
-841.6 + .093 T + .031 T LOG P(SO2)	-16966.1/T + 1.880 + .631 LOG P(SO2)
-845.9 + .137 T + .031 T LOG P(SO2)	-17053.9/T + 2.758 + .631 LOG P(SO2)
-848.9 + .151 T + .031 T LOG P(SO2)	-17112.7/T + 3.053 + .631 LOG P(SO2)
-851.8 + .161 T + .031 T LOG P(SO2)	-17171.3/T + 3.249 + .631 LOG P(SO2)
-857.2 + .172 T + .031 T LOG P(SO2)	-17281.2/T + 3.469 + .631 LOG P(SO2)
-839.7 + .155 T + .031 T LOG P(SO2)	-16928.3/T + 3.116 + .631 LOG P(SO2)
-876.3 + .104 T + .030 T LOG P(SO2)	-17665.7/T + 2.089 + .600 LOG P(SO2)
-880.7 + .148 T + .030 T LOG P(SO2)	-17754.6/T + 2.979 + .600 LOG P(SO2)
-883.3 + .161 T + .030 T LOG P(SO2)	-17806.0/T + 3.236 + .600 LOG P(SO2)
-885.1 + .167 T + .030 T LOG P(SO2)	-17843.3/T + 3.362 + .600 LOG P(SO2)
-892.4 + .184 T + .030 T LOG P(SO2)	-17989.6/T + 3.717 + .600 LOG P(SO2)
-892.1 + .184 T + .030 T LOG P(SO2)	-17983.4/T + 3.705 + .600 LOG P(SO2)
-886.0 + .178 T + .030 T LOG P(SO2)	-17862.1/T + 3.584 + .600 LOG P(SO2)
-936.4 + .212 T + .030 T LOG P(SO2)	-18877.1/T + 4.277 + .600 LOG P(SO2)
-935.6 + .212 T + .030 T LOG P(SO2)	-18861.1/T + 4.269 + .600 LOG P(SO2)

equilibrium conditions of the considered reactions

(see page 9)

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<u>5 a</u> (n° 2787)	<u>temperature from zero to 1500°K,</u> <u>E from -1.70 to +0.20 volt_{soe}.....</u>	47				
<u>5 b</u> (n° 2788)	<u>temperature from 890°K to 1070°K,</u> <u>E from -0.10 to +0.02 volt_{soe}.....</u>	48				
<u>FIGURE 6</u> (n° 2757)	<u>Conditions of stability of iron salts and of</u> <u>iron oxides and iron in the presence of dry</u> <u>air polluted by (SO_3), (SO_2) or sulphur vapor</u> <u>for different partial pressures of $(SO_3) + (SO_2)$</u> <u>+ (S_{total}):</u> <table><tr><td><u>a. 10^{-6} atm.</u></td><td><u>b. 10^{-4} atm.</u></td></tr><tr><td><u>c. 10^{-2} atm.</u></td><td><u>d. 1 atm.</u></td></tr></table>	<u>a. 10^{-6} atm.</u>	<u>b. 10^{-4} atm.</u>	<u>c. 10^{-2} atm.</u>	<u>d. 1 atm.</u>	49
<u>a. 10^{-6} atm.</u>	<u>b. 10^{-4} atm.</u>					
<u>c. 10^{-2} atm.</u>	<u>d. 1 atm.</u>					

B-43 Blank

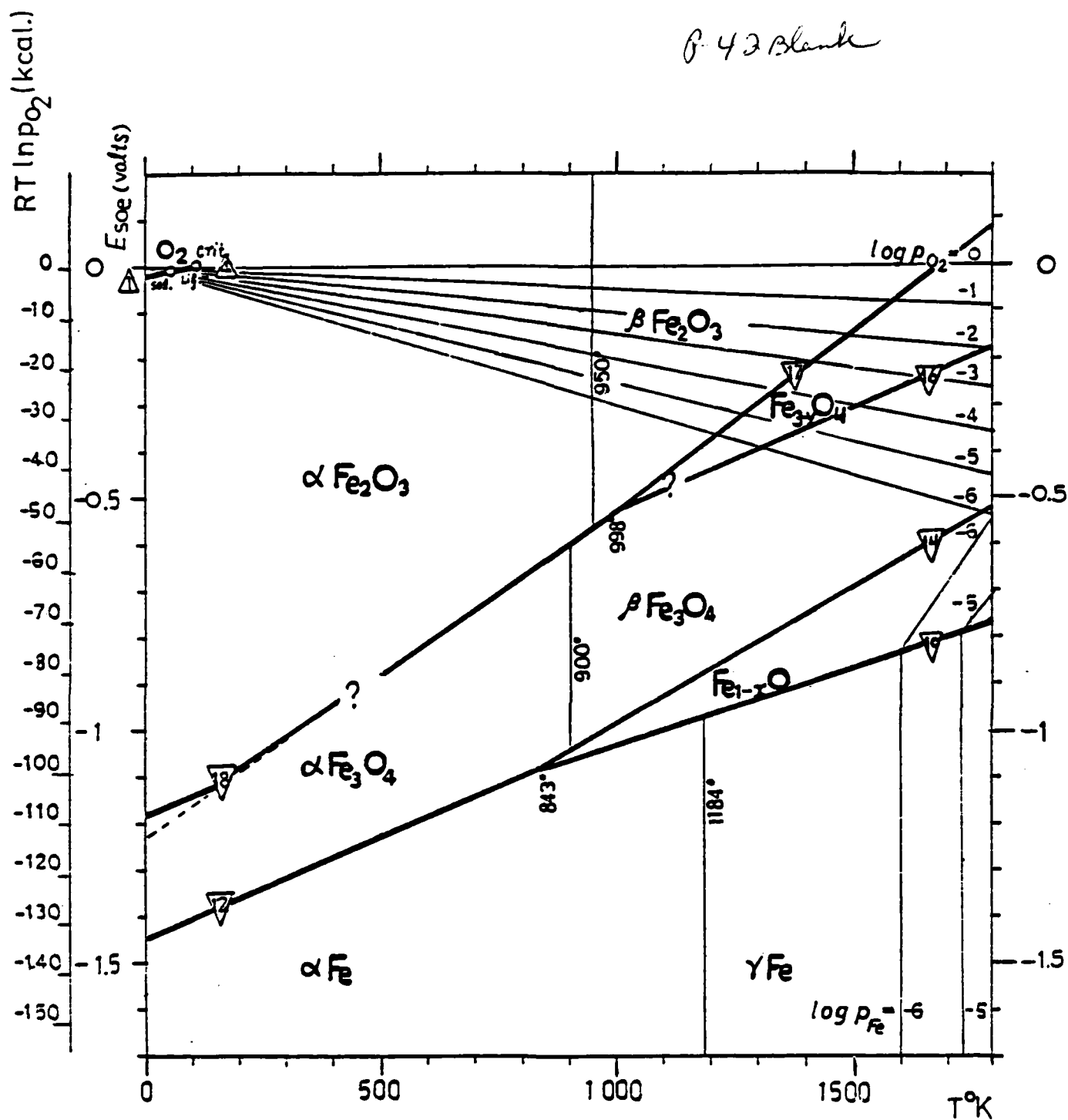


FIGURE 1 Equilibrium diagram $E = f(T)$ for the system O-Fe
(temperature from zero to 1800°K, E from -1.70
to +0.20 volt_{soe})

MP.2621 020884 2784

(see page 9)

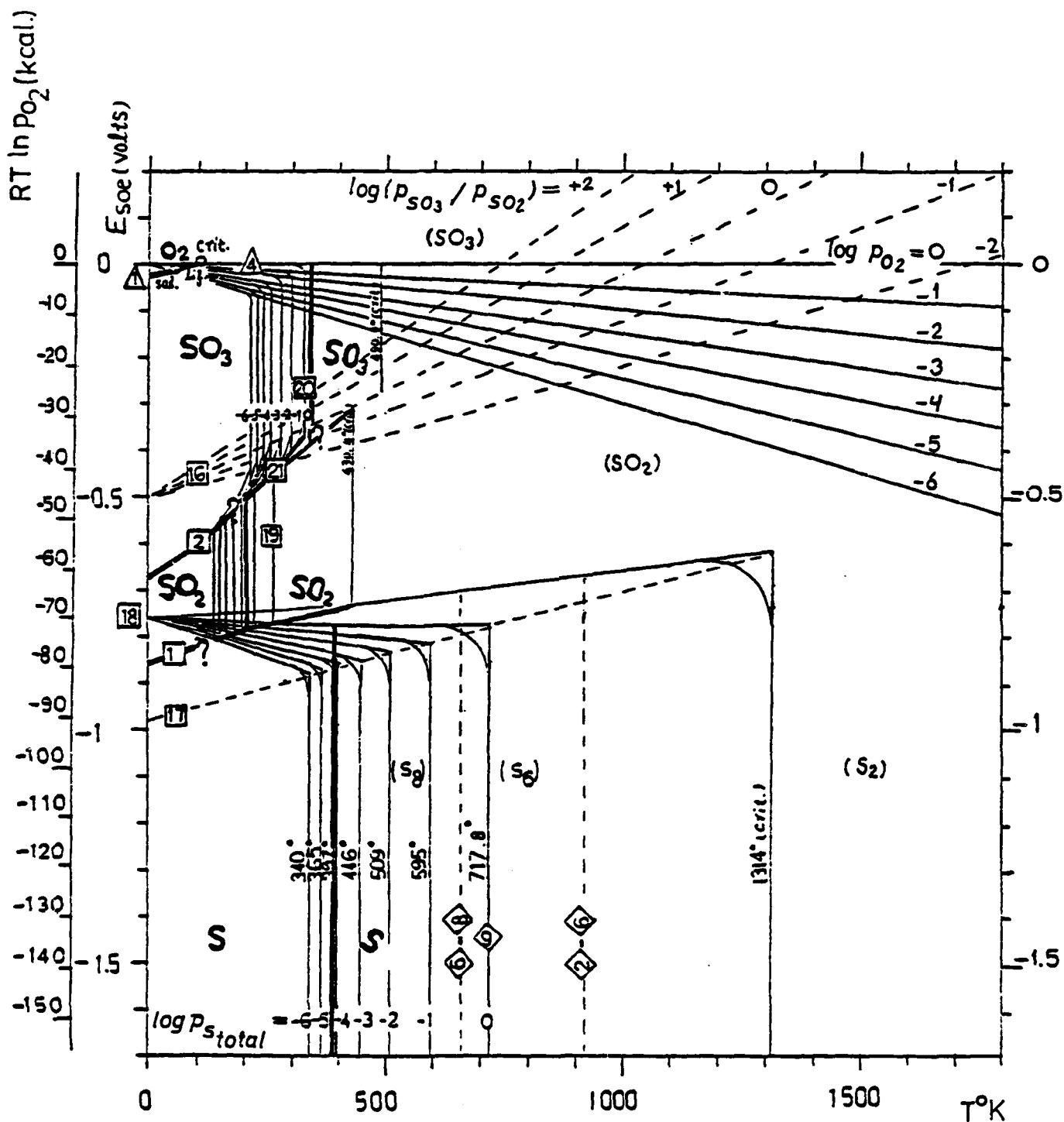


FIGURE 2 Equilibrium diagram $E = f(T)$ for the system O-S
(temperature from zero to 1800°K, E from -1.70
to + 0.20 volt_{soe})

MP.2621 050884 2785

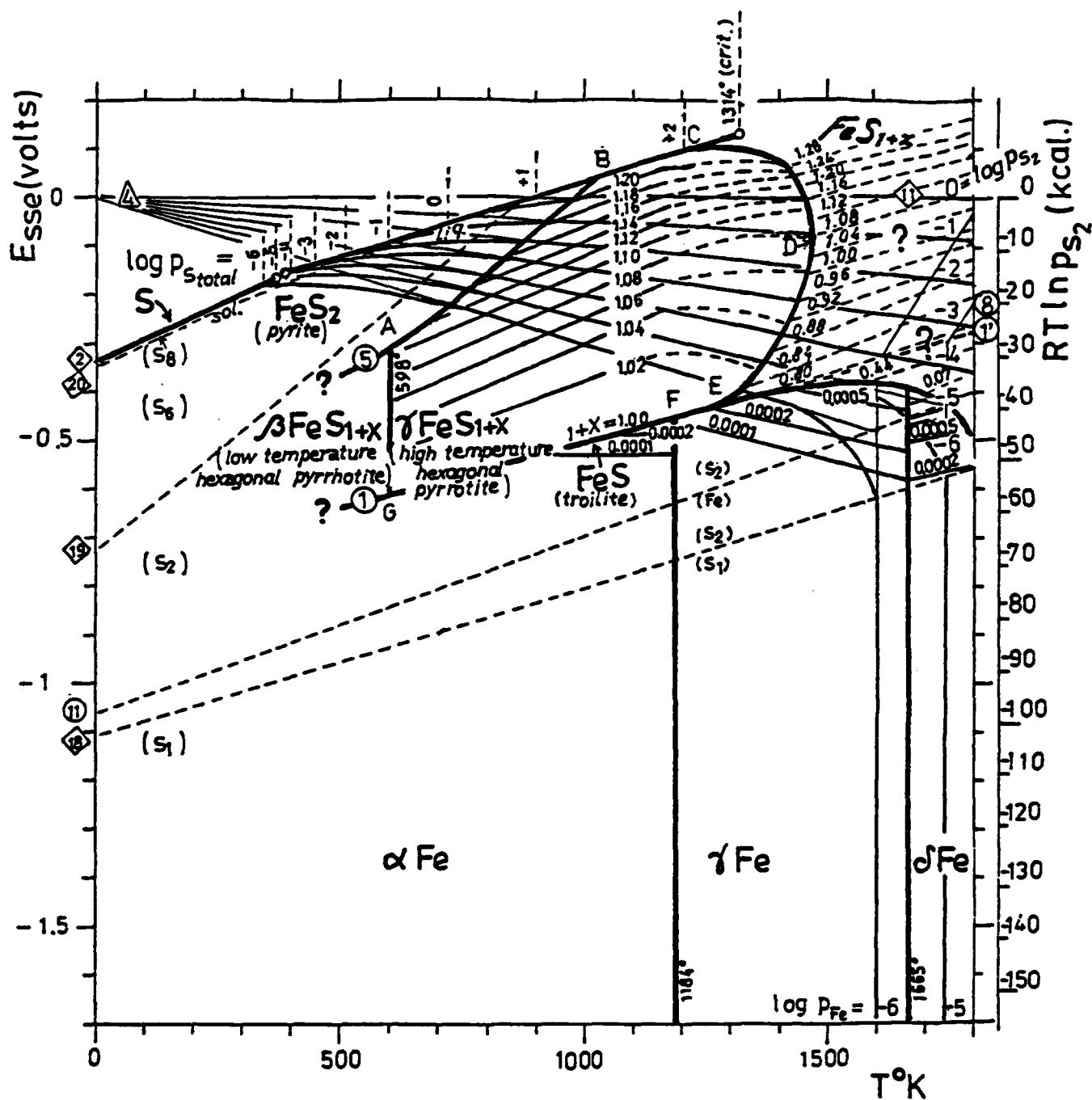


FIGURE 3 Equilibrium diagram $E=f(T)$ for the system
S-Fe (temperature from zero to 1800°K,
 E from -1.70 to +0.20 volt_{ss})

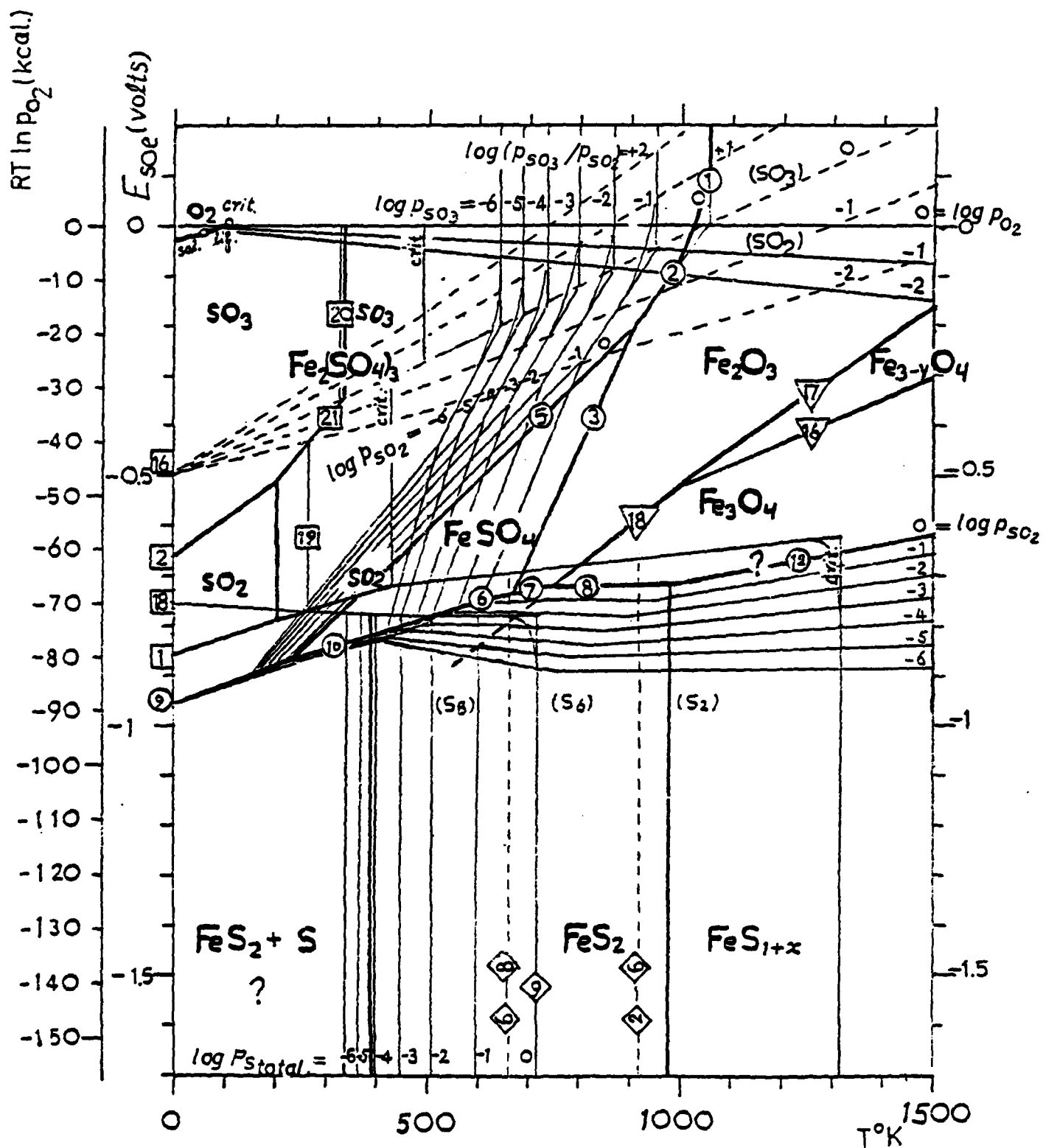


FIGURE 4 Equilibrium diagram $E = f(T)$ for the system
 O-S-Fe (temperature from zero to 1500°K,
 E from -1.70 to +0.20 volt_{soe})

MP.2609 100884 2756

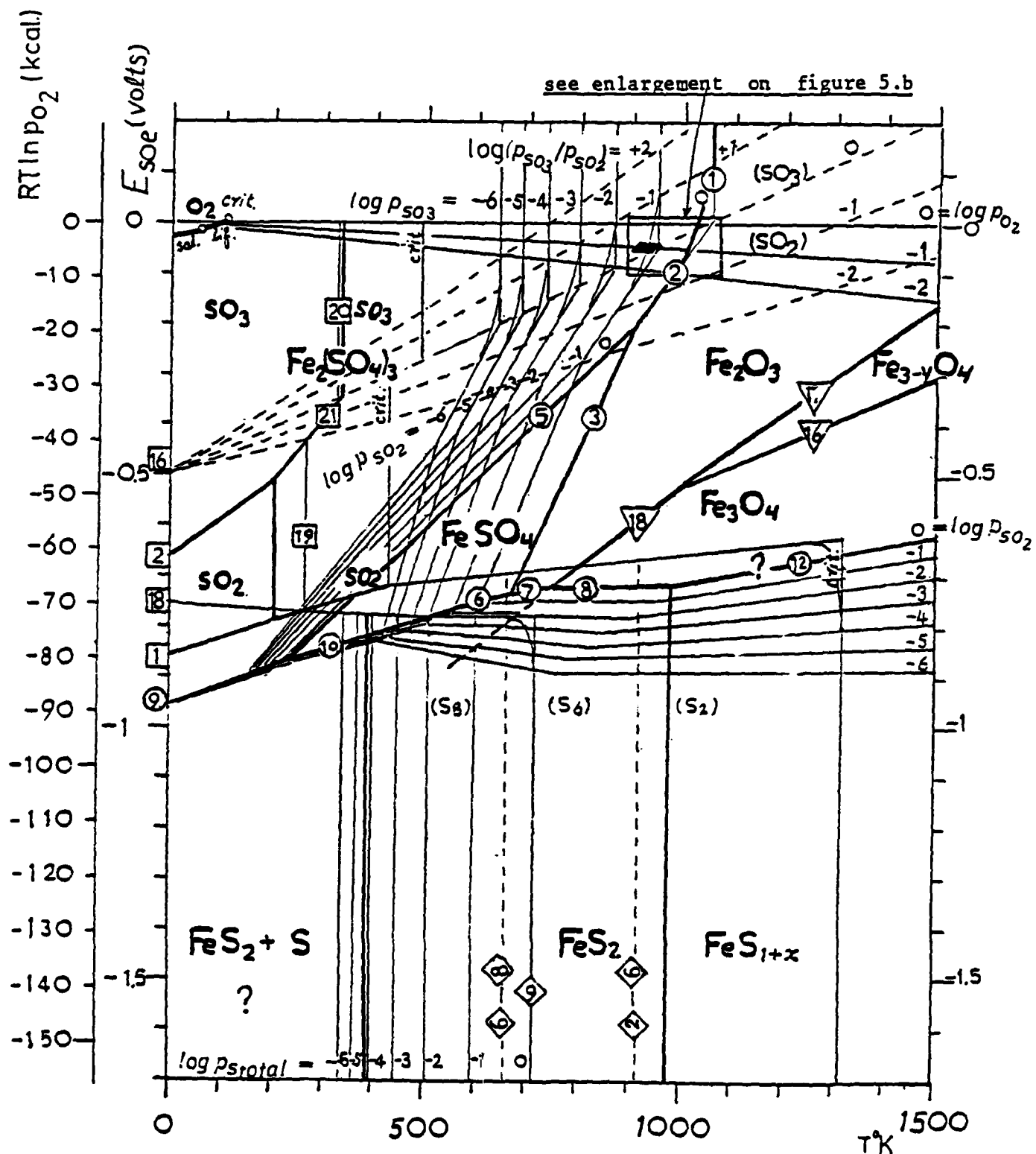


FIGURE 5a Condition of catalytic activity of Fe_2O_3 for the oxidation of (SO_2) to (SO_3) temperature from zero to $1500^\circ K$, E from -1.70 to $+0.20$ volt_{soe}

MP.2621 150884 2787

(see page 13)

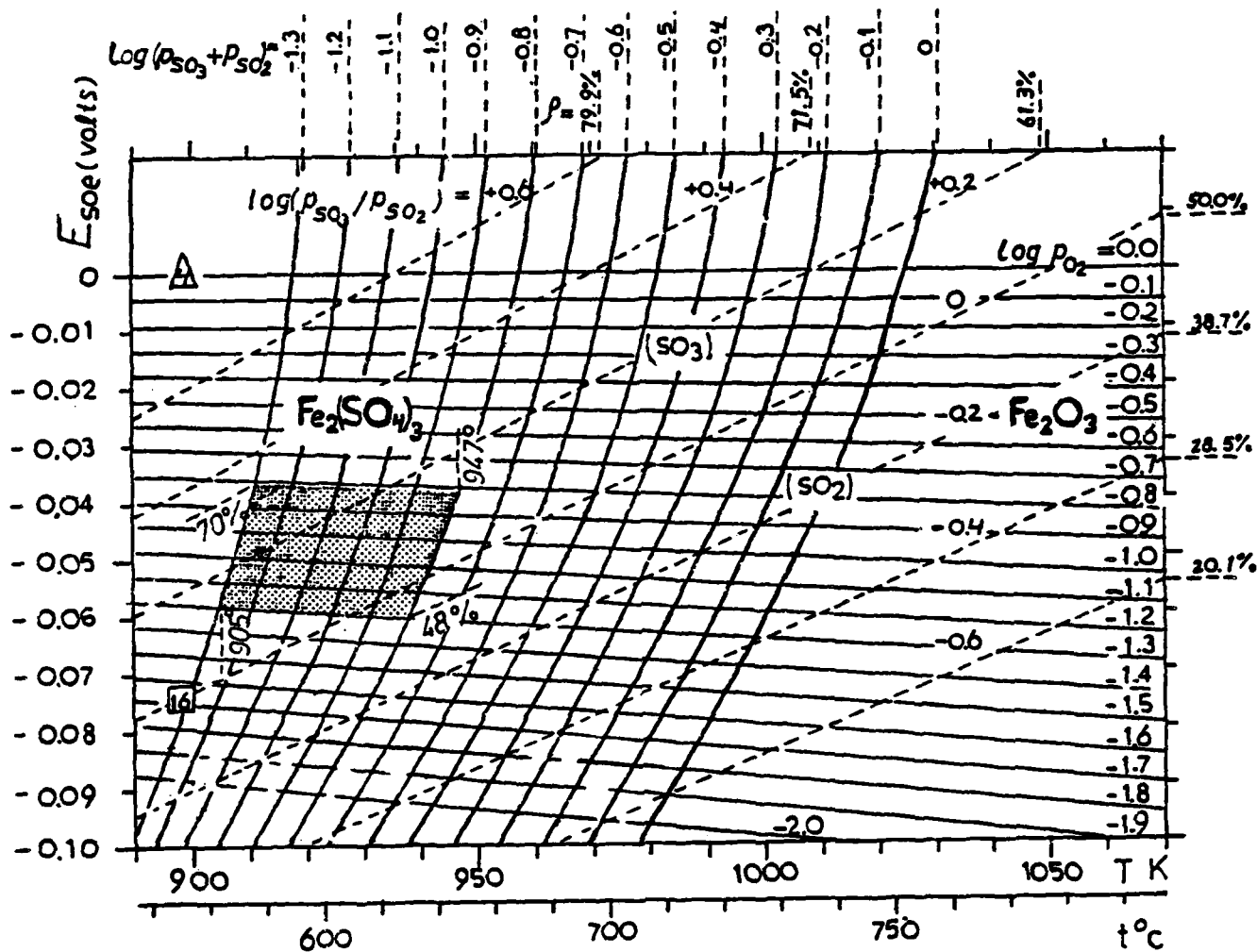


FIGURE 5b Conditions of catalytic activity of Fe_2O_3
for the oxidation of (SO_2) to (SO_3)
temperature from 890°K to 1070°K,
 E from -0.10 to +0.02 volt_{soe}

MP.2671 130884 2788

(see page 13)

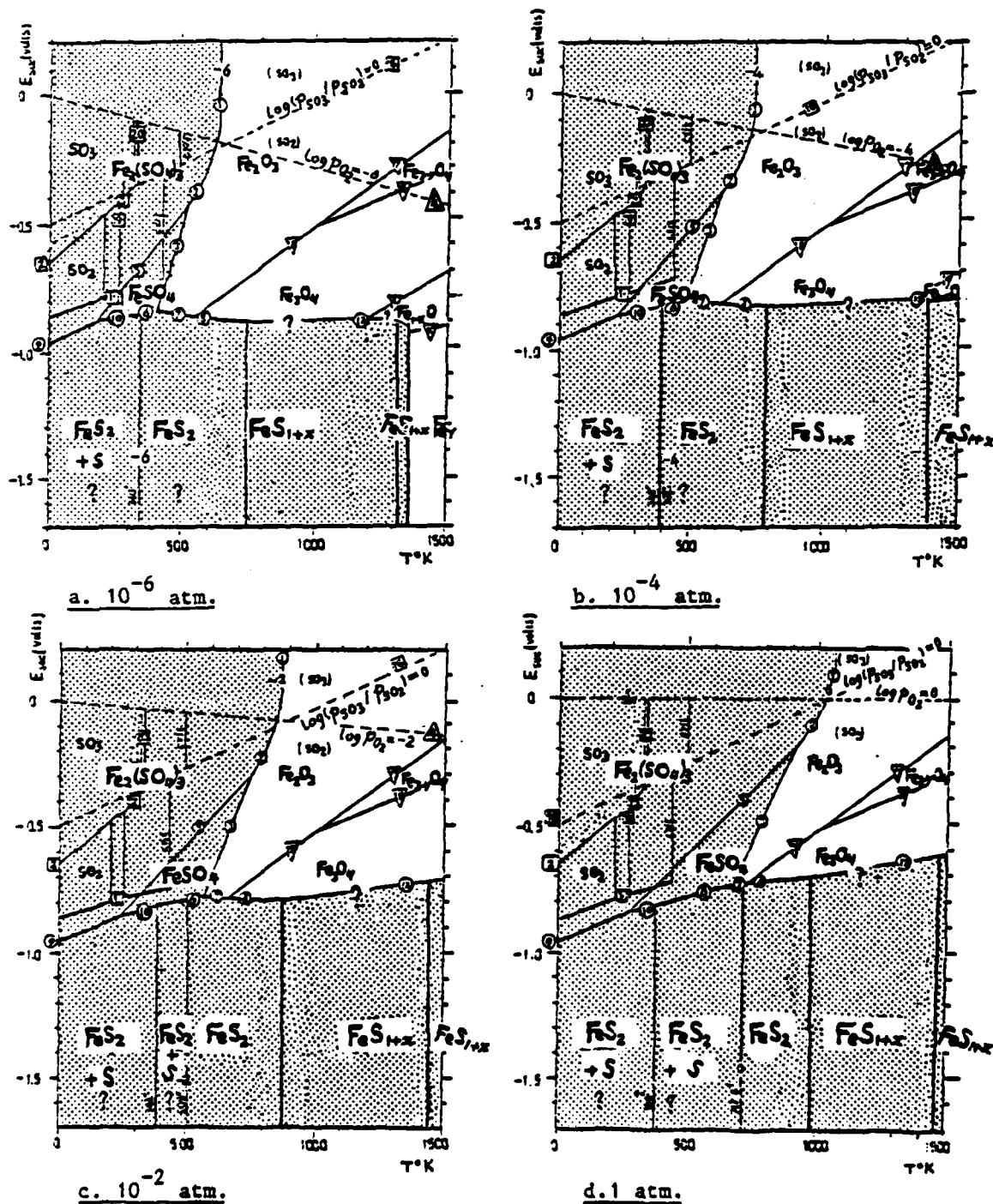


FIGURE 6 Conditions of stability of iron salts and of iron oxides and iron in the presence of dry air polluted by (SO_3) , (SO_2) or sulphur vapor for different partial pressures of $(SO_3)+(SO_2)+(S_{total})$

END

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